SYNTHESIS, PROCESS PARAMETER CONTROL AND PERFORMANCE OF NANO CERAMIC COATINGS FOR DIESEL ENGINE APPLICATIONS

Synopsis submitted to CHRIST (Deemed to be University)

as partial requirement for the award of the Degree of

DOCTOR OF PHILOSOPHY

IN

MECHANICAL ENGINEERING

by

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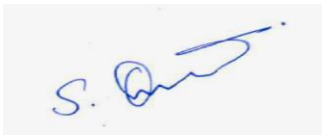

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SEPTEMBER 2022

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ABSTRACT

Ceramics are non-metallic inorganic solids which are used in various forms (bulk & coatings) and in environments (low & high temperature) to provide protection from thermal, wear or chemical attack. Due to their high melting point, compressive strength, oxidation and corrosion resistant properties ceramics are strong, hard, brittle and harsh environment resistant. Ceramic coatings are generally applied on metal components to either enhance their life or augment the performance of the devices they are mounted on. Furthermore, coatings being thin (few small units to hundreds of microns); they do not demand significant alteration in component design. Among the many types of coatings used in engineering applications, Thermal Barrier Coatings (TBCs) and wear resistant coatings (WRCs) are used to protect metallic components from thermal and mechanical damages respectively. 6 to 8%Yttria stabilized zirconia (6-8% Y_2O_3-ZrO_2), generally designated as 8YSZ has been extensively used as TBCs and alpha alumina (α-Al_2O_3) find applications as WRCs. 250 to 300µm thick micron grained TBCs, with grain sizes typically up to 20 µm or even higher are well known to thermally insulate diesel engine combustion chamber to provide enhanced fuel efficiency characteristics. The coatings also find use in power plants, textiles, automotive and aero-space industries etc. to provide benefits like improved product quality & energy efficiency, extended wear life, reduced maintenance cycles and costs etc.

Among ceramic coatings, nanostructured coatings have received further interest because of their extraordinary properties including enhanced hardness, strength, ductility, and toughness when compared with coatings with micron grained microstructure. Nanostructured zirconia is also expected to serve as advanced TBCs in engine applications, although the information is mostly classified. Similarly, nano alumina ceramic coatings too when applied on engineering parts have the potential to highly improve their wear life. Nano coatings are also expected to give improved performance compared to their microns grained counterpart coatings at reduced thicknesses (~150µm thick nano grained vs ~250µm thick micron grained). Nevertheless, difficulty lies in the complex nature of nano grained coatings synthesis.

Atmospheric Plasma Spray (APS) coating technique, one form of thermally sprayed coatings may be a viable tool for fabrication of several tens of microns thick nano-structured coatings that may be suitable for industrial applications. For APS, nano-sized powders need to be densified without the loss of their nanostructure to obtain bulk products/coatings. Reportedly

various factors affect the coatings properties: composition, particle size, and process methodologies that directly influence the structural stability, microstructure and thickness of the coatings. Yet, APS system is widely used for development of industrial grade coatings including nano structures. However, being classified information; details of the processes to generate nano structured coatings through APS are not widely published.

APS requires feedstock powders of well-framed specifications to develop high quality coatings. The sprayable powders freely flow through the high temperature plasma under controlled conditions to deposit on substrates or components placed in the "line of sight" of the plasma. The challenges in plasma spray coating nano-materials are to (1) make the nano sized feed powder to flow freely and uniformly through the plasma and to (2) retain the nanostructure of the feedstock (nano particles agglomerated to microns sizes) in the coating. If the feed powder does not flow easily through the plasma, isolated patches of non-uniform deposition are found on the substrate. If the nanostructured powder particles are completely melted during spraying, the traditional behavior of powder particles such as solidification, nucleation and growth will take place when subjected to high heat conditions which destroy the intended nano-microstructure. During plasma spraying of nanostructured ceramics it is necessary to only superficially melt the surface of the powder particles to achieve the necessary physical conditions for good cohesion and adhesion. Low densities of nano powders make the task extremely challenging.

One method to synthesise APS feedstock powders is spray drying where, with optimized process parameters nano powders can be agglomerated into free flowing powders. It is a process of conversion of particles from slurry form into agglomerated particles of desired sizes controlled by binder addition, spray dryer settings (temperature, voltage, flow rate etc.).

Keeping the above background in view, the main goal of this research was to develop ceramic coatings with nano microstructures to serve as thermal barrier and wear resistant coatings followed by the determination of their suitability for application in diesel engine to enhance its performance. The following were the three major objectives.

(a) Synthesis of free flowing plasma sprayable powders from nano ceramic powders.
(b) Synthesis of 150 to 180µ thick coatings with nano grained microstructure from the synthesized plasma sprayable powders and application on diesel engine components.
(c) Establishment of "proof of concept" of using nano coatings to enhance performance of single cylinder diesel engine.

The details are described below.

Nano powders of (a) $8Y_2O_3$-ZrO_2 (8YSZ) and (b) α-Al_2O_3 were the starting materials used. 8YSZ nano grained coatings were meant to provide thermal protection to Al-Si pistons and to improve the performance of the engine. α-Al_2O_3 nano ceramic coatings was aimed to enhance the wear resistance of steel components in the diesel engine. TBCs generally are formed to a thickness of a couple of hundred microns on combustion chamber components to retain the heat within itself. α- Al_2O_3 is a well-known oxidation and wear resistant material for use in high heat and mechanical damage prone applications. Tolerance levels in automotive components pose major challenges for use of coatings (due to additional layers). Extremely small gaps between parts in action in the automobile demand the need for effective coatings but with very small thicknesses. Expected to be realized only by the use of nano structured ceramic coatings of suitable compositions, the goals were achieved by the following major developmental stages.

(a) Micron sized plasma sprayable powders synthesis from $8Y_2O_3$-ZrO_2 (8YSZ) and α-Al_2O_3 nano powders, by two methods: (a) manual agglomeration and (b) spray drying by using laboratory and pilot plant scale spray dryers; and optimisation of spray drying parameters, their characterization and confirmation of their suitability for use in APS systems.

(b) 8YSZ nano particles synthesis in laboratory scale by sol-gel method, to ensure the raw material supply chain.

(d) Plasma sprayed nano ceramic coatings deposition on stainless steel and aluminium-silicon plates, their characterization and development of optimized plasma spray coating parameters to attain good quality coatings and application on actual engine components.

(i) Performance evaluation of the modified engine (coated components: 8YSZ on Al-Si piston head & α-Al_2O_3 on steel gudgeon pin) and comparison with baseline (un-modified) engine.

<u>The experimental details of the above developmental work are summarised below.</u>

(a) Nano powders of 8YSZ and α-Al_2O_3 (commercial) were spray dried with organic binders (polyvinyl alcohol-PVA) to form micron sized agglomerates (plasma sprayable powder) to be used as the feedstock for the APS equipment. Spray drying parameters were optimised for spray dried powder output with respect to starting nano powder quantity (high yield) and flowability.

(b) 8YSZ nano powders were synthesized in the lab using sol-gel method with zirconium oxy chloride and yttrium nitrate as precursors, citric acid as chelating agent and ethylene glycol for the divergence reaction followed by calcination @ 1000℃.

(c) The plasma sprayable powder (agglomerates of nano powders) while flowing through the plasma, disintegrated into their constituent nano particles and formed nano-structured plasma spray coatings on the chosen metal substrates pre-coated with commercial NiCrAlY (METCO, USA) bond coat. The nano coating deposition comprised of significant developmental efforts involving optimization of spray coating parameters for optimum coating properties.

(d) The plasma sprayable powders were characterized for size by sieve analysis (ASTM D6913/D6913M-17), grain morphology by Scanning Electron Microscopy (SEM) and flowability by hall flow meter. The 8YSZ nano powders were analysed for structural phase via X-Ray Diffractometry (XRD), particle size and chemical composition by SEM and Energy Dispersive X-ray spectroscopy (EDS). The sprayable powders were also evaluated for free flowability and deposition efficiency by using APS equipment with carrier gas, without generating the plasma arc.

(e) The nano-structured coatings were characterised for structural phases via XRD, microstructure & chemical composition by SEM & EDS, thickness by cross section metallography, determination of temperature drop across coating thickness by thermal barrier test, thermal fatigue tests to evaluate coatings adhesion quality under high temperature environment, evaluation of mechanical properties by wear resistance, hardness and scratch adhesion test.

(f) The coatings were evaluated further by incorporating the coated components in a 5HP, 1500 RPM, four stroke single cylinder diesel engine (Kirloskar Oil Engines Limited make) and by performing an engine test under actual engine working conditions. The coated components were ~ 150 µm thick coatings of nano 8YSZ and nano α-Al_2O_3: each deposited on Al-Si alloy piston head and steel gudgeon pin respectively (~75 µm NiCrAlY bond coat). The engine was run for 100 hours under maximum load condition; the fuel and thermal efficiency were measured. Visual inspection of the coated components at the end of performance tests revealed the coatings condition.

<u>Major findings from the above work are listed below.</u>

a) Micron sized free flowing plasma sprayable powders of (a) 8YSZ and (b) α-Al_2O_3 grains

were found to be suitable for injection into the APS plasma stream. Powder output obtained through (a) manual method and (b) spray drying methods were 70 and 50 grams/batch respectively with similar flowability rates of 46 to 48 grams/ minute, and similar particle sizes between 50 and 110µ for both 8YSZ and α-Al_2O_3. (i) Optimised spray drying parameters & (ii) publication of an Indian patent are the major outcomes.

b) Sol-gel synthesis of 8YSZ powder particles, prepared from 1 litre of distilled water with precursors yielded the gel in 7 to 8 hours. It was calcined at 1000℃ to yield 80 grams of nano crystalline powders per batch. The particle sizes were between 30 and 90nm (SEM). EDS and XRD analysis confirmed the presence of Zr, Y & O and major tetragonal ZrO_2 (t-ZrO_2) phase with minor (<5%) phase of monoclinic ZrO_2 (m-ZrO_2) respectively.

c) The sprayable powders (8YSZ & α-Al_2O_3) when fed through high temperature plasma in APS, under optimised spray conditions resulted in plasma sprayed coatings with nano grained microstructures. Phases (XRD) obtained in the coatings were t-ZrO_2 & α-Al_2O_3 respectively, with average grain sizes between 30 & 50nm (SEM). EDS confirmed the presence of corresponding elements (Y, O & Zr, and Al & O). The top coat thickness (measured by cross section metallography & SEM) was up to (a) ~170 µ in 8YSZ and (b) ~ 150µ in α-Al_2O_3 coatings. An Indian patent has been published based on this work.

d) The SS/8YSZ coatings withstood 500 thermal fatigue cycles, between 900℃ (gas flame) & ambient at room temperature (test stopped before failure). Similarly, the Al-Si/8YSZ coatings when cycled between 500℃ and the ambient also withstood 500 thermal shock (fatigue) cycles. Intact coating, uniform microstructure with marginal grain growth after thermal fatigue tests was observed (~90nm in SS/8YSZ & ~70nm in Al-Si/8YSZ).

e) The coating thickness is a function of the number of passes, although at higher thicknesses the cohesion between the layers is negatively affected. SS/8YSZ top coat thickness was developed at about 10µm per pass that was stable up to a maximum of ~200 µm. In 8YSZ TBC, at thickness >170µm, flaking of coating was observed and hence the study was restricted to 170µm thick coatings. Thickness build up on Al-Si was restricted to a maximum top coat thickness of only 130µm. No change in the crystalline structure or destabilization of the t-ZrO_2 phase was found after thermal fatigue tests.

f) Temperature drop (ΔT) across a ~150µm thick 8YSZ coating was determined to be 40℃ on the metal (SS) side when the ceramic was exposed to gas flame at 1000℃.

g) Wear percentage loss of α-Al_2O_3 coatings on the substrates (SS and Al-Si) were marginal

although varied (being a function of the applied load), confirmed the suitability of the nano alumina coatings for wear resistant applications. This was further corroborated via the hardness number of the coatings which was found to be between 980 HV and 1010 HV at a load of 50 grams on Al-Si and SS substrate respectively. In the scratch adhesion test on (a) Al-Si/8YSZ the average depth of ~ 17.9 µ, average friction of ~ 3.45 N and in (b) SS/α-Al_2O_3 the average depth of ~ 18.8 µ and average friction of ~ 3.11 N was obtained. The indenter penetrated only 10% of the thickness of coating confirming the good quality of coating strength and hardness. This was confirmed via the hardness tests as well. The medium friction values supported the viability and potential for the coatings to be applied on engine components with fine tolerance, to avoid rubbing while in motion.

h) The 8YSZ coated piston withstood the 100 hours of engine performance evaluation at maximum load and exhibited performance shows the BSFC reduced up to 22%BSFC and correspondingly other beneficial outcomes (higher thermal efficiency etc.). This was a major achievement and a highly significant outcome of the project. An Indian patent has been published on this novel finding.

i) Nano α-Al_2O_3 coated gudgeon pin withstood 100 hours of diesel engine test run at maximum load without any deterioration in coating quality.

Total of 4 patents were published based on this work pertained to fabrication of ceramic coatings with nano grained microstructure.

Further details of the above work are described in the following sections.

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1. INTRODUCTION

Surface engineering may be defined as “The design of outer surface and underlying substrate together as a conveniently arranged system- to give a cost effective performance enhancement of which neither is capable on its own”. The goal is to manipulate appropriate technologies to achieve optimal surface property designs for specific applications in the most cost effective manner. In basic terms it is the application of a coating to the surface that needs protection. The coating is the covering that is applied to the surface of an object (component): the object is usually referred to as the substrate. The purpose of applying the coating may be decorative, functional, or both. The coating itself may completely or only partly cover the substrate. Functional coatings may be applied to change the surface properties of the substrate with a specific purpose: such as to provide protection from thermal or electrical damage, increase corrosion or wear resistance etc. Materials /compositions play a significant role in deciding the suitability of a coating for the identified application. Ceramics are non-metallic inorganic solids, which can withstand extreme low or high temperatures, wear, chemically harsh environment etc. Ceramics are strong, hard and brittle; possess high melting point, compressive strength, oxidation and corrosion resistance. Hence they are applied on metal components to protect their outermost surfaces from harsh engineering environments.

Among the coating materials, nano-ceramics are finding wide application due to the unusually favorable microstructures leading to improved properties: toughness, thermal shock and wear resistance etc. With regard to surface engineering applications involving coated components, methodologies such as thermal spray coatings are widely applicable in almost all engineering industries: with enormous potential for use in the automotive sector and also offers new possibilities to prepare coatings with nano-microstructures. Plasma spray coating, a thermal spray technology tool is an excellent tool for ceramic coatings applications: Controlling the material structure at nano meter level is expected to bring revolutionary improvements in the coating properties.

In thermal spray coatings process the coating material spray powder/particles are accelerated to flow through the flame or plasma as the case may be. The particles melt (totally or partially), before impacting onto the prepared substrate where they flatten and form flattened lamellae, called splats, and form the layers which lead to coating build up. Particles melting occur in rather short times (a few milliseconds) and their solidification in even shorter times (a few microseconds) with strong temperature gradients and cooling rates resulting sometimes in meta stable or amorphous phases. The coating microstructure is very complex with many features such as voids, cracks (intra-lamellar failures), delamination

(inter-lamellar failures), and interfaces of different length scales. Thus, the coating properties not only depend on the powder morphology, even if it is an important parameter, but also on the powder processing conditions.

Generally, thermal /plasma spray powders are manufactured using several different techniques, including agglomeration, sintering, fusion & plasma densification. The resulting powder must have very uniform chemistry and strict size control that will produce high quality ceramic coatings. The powders must deliver good spray performance and value for all types of applications involving wear and corrosion resistance, thermal insulation and electrical insulation. The powder feedstock morphology and particles size distribution are related to its manufacturing route and thickness build-up, which in plasma spray coating processes, they are few tens of microns. However, powders with nano sized grains have gained importance because nano particles offer significantly superior advantages over the same composition but with micron sized grain morphologies.

Studies and developmental work related with nano-structured coatings for which nanometer-sized particles or particles susceptible to form nanometer-sized structures upon cooling have been undertaken since the beginning of this century, especially keeping the industrial applications in view. Most of the earlier nano-scale coatings were developed in the lab scale and suited on small specimen and proto types alone. Furthermore, any industrial scale developments were mostly maintained as classified information. The main challenges in thermal spraying nano-materials are to

i. Make the nano sized feed powder to flow freely through the high temperature plasma and
ii. Retain the nanostructure of the feedstock (agglomerated to tens of microns sizes) in the deposit (coating) as well.

Nano-powder normally cannot be processed by traditional powder metallurgical methods because of their high surface area and active interaction with the surrounding environment. Since the early stages of thermal spray, it has been recognized that the powder composition, size distribution, shape, mass density, mechanical resistance etc. play a key role in coating microstructure and thermo mechanical properties. The principal characteristics of particles are strongly linked to the manufacturing process. Thermal spray coatings qualities also depend on the process used to spray the particles and spray parameters. Many papers have been devoted to the relationships existing between coating properties and structures at different scales and manufacturing processes. Conventional spray conditions are governed by good powder flowability and dense particles to generate micro-metric structures.

The sub-micron/nano sized ceramic powders (<1μm) cannot be sprayed by particle

injection into the plasma as it lacks the momentum necessary to penetrate into the plasma or to impinge on the surface while the plasma sweeps over the substrate. If the feed powder does not flow easily through the plasma, isolated patches of non-uniform deposition are found on the substrate. If the nano-structured powder particles are completely melted during spraying, the traditional behavior of thermal spray particles, such as solidification, nucleation, and growth will take place. Such processes will destroy the original nano-structured features of the feedstock. During spraying if nano-structured powder particles are completely molten; the normal behavior of the spray particles, such as solidification, nucleation and growth will take place. Such processes will destroy the nano-structured features of the feedstock. During plasma spraying of nano-structured ceramics it is necessary to partially melt the powder particles to achieve the necessary physical conditions for cohesion and adhesion.

In order to fulfill plasma spray process requirements, it is essential to have suitable particle size, morphology and density although, in this process, the advantageous property due to large surface area of nanoparticles is lost to some extent. Hence for the coating to be performed, it has been found that the powder should consist of dense agglomerated particles in the size ranging from 10-20 μm in diameter with bulk density of around 1.7 g/cc. Hence, it becomes necessary to process the processed nano particles to achieve appropriate size range.

Spray drying is a process by which a fluid feed material (slurry) is transformed into a dry powder by spraying it into a hot medium. It is also considered to be the best technique used for agglomerating nano powders. They can be used as the raw materials (feedstock) for plasma spray coating. When making agglomerated powders, the slurry (i.e.) the water based suspension has to be atomized into the discrete droplets in a hot drying medium. The water present in the suspension will be evaporated due to the large surface area to volume ratio of the droplets, thereby resulting in dry agglomerated powder. Various parameters such as droplet size, atomizer design, solid loading, pH of the slurry, hot air inlet and exit temperature, atomizing air flow rate and feed rate of the slurry control the morphology of the granules. Among all the parameters, the most important parameter to be considered is the slurry preparation. The factors which govern the slurry preparation are the percentage of solid loading, binder, the dispersant and its pH's of the slurry. The binder which is most suitable for the study is (Poly vinyl alcohol) and varying the percentages of both the solid loading (ZrO_2) and the binder at different pH values must be tried out since it has been established in literature that percentage of binder plays a vital role in the agglomerated powder quality.

The atomizing air flow rate and feed rate of the slurry also has an effective influence on particle sizes whereas the slurry flocculation is expected to control the tapped density and

flowability values. The spray dried particles are usually spherical and free flowing in nature and which allows the ease with which the plasma spraying process can be carried out and these powders can be easily fed by the plasma spray gun. Plasma spray coatings prepared from these powders are expected to possess higher thermal shock resistance than those coatings whose powders were prepared by precipitation, sintering/crushing. It is envisaged that good quality powders can be accomplished by spray drying the slurry consisting of appropriate concentration of solid loading of the chosen ceramics, dispersant and the binder.

Furthermore, keeping an end application in mind, it is mandatory that the developed nano-ceramic coatings possess all the best properties (adhesion, cohesion, mechanical and thermal characteristics, homogeneity etc.) when they are plasma sprayed onto metals or alloys as the substrates as well. One interesting application where the ceramic nano coatings may be applied for good use may be in the automotive sector. While coatings of suitable materials and other properties are likely to significantly improve the functionality of automotive components, one big challenge in application involving coatings on automotive components is their tolerance levels. Extremely small gaps between parts in action in the automobile demand the need for extremely effective and yet coatings with very small thicknesses. This can be achieved by the use of nano structured ceramic coatings. In addition to a fine microstructure, nano-structured ceramic coatings possess extraordinary properties when compared with their micron sized counterpart coatings. Difficulty lies in the fact related with the complex nature of synthesis where for most industrial applications these nano-sized powders need to be densified without the loss of their nanostructure to obtain bulk products. Each and every technique has its own advantages and disadvantages.

Two primary factors that govern the automotive sector are (a) light weighted components to reduce vehicle inertia mass (b) emissions control. In addition, the dream of manufacturing and running an automobile without lubricants is expected to be realized in future through surface engineered coatings. Automotive weight reduction is regarded as one of the most effective means for decreasing fuel consumption. Lighter materials are being studied extensively to replace the steels: prime candidate being aluminium alloys have begun to be used for various automotive parts for its low specific gravity (approximately 1/3 of steel). The use of aluminium alloy is not only limited to conventional castings such as engine blocks, but extends to hoods, trunk lids, outer panels like doors and protective covers like heat insulators.

Nearly 15 % of the power supplied to an IC engine is wasted due to friction between contacting mechanical parts in relative motion and >25% in the form of heat energy. Most of the friction is caused by cylinder liner/piston –piston rings with crank pin, injection pump and

valve train also being responsible for mechanical dissipations. Traditionally cast iron is used as material for engine block. Nevertheless Aluminium alloys have significant potential to be introduced in automobile industries to reduce the vehicle inertia mass. Tribological Coatings are required for automotive components to improve wear resistant and seizure properties, thus ensuring useful service life. TBCs on aluminium alloys engine components are used to improve the combustion characteristics (increase performance, efficiency & control pollution).

Keeping the above background in view, the aim of the present research work was to fabricate ceramic nano-coatings by using plasma spray coating methodology and to use the developed coating for different automotive applications. Nano ceramic coatings exhibit significantly superior properties to their thicker counterparts such as microns thick coatings and it is this challenging aspect of development of nano-ceramic coatings on aluminium base material which was taken up in this research. APS technique was employed to prepare the nano ceramic coatings (6-8%Y_2O_3-ZrO_2 for TBC and α-Al_2O_3 to serve as wear resistant coatings).

The focus was on process development of (a) plasma sprayable powders synthesis from commercial nano- ceramics (8YSZ and α-Al_2O_3) powders (b) Plasma sprayed coatings of these powders on steel and aluminium alloy substrates and (c) spray powder and coatings characterization and to finally (d) assess the potential of their utilization in chosen automotive components. The work was concentrated on applications involving nano grained 8YSZ thermal barrier coatings and α-Al_2O_3 wear resistant coatings specifically suited for aluminium and steel based automotive components.

2. EXTENSIVE LITERATURE REVIEW

Summaries of few journals papers (typical) pertaining to my research that were reviewed are given below.

1. Joanna Spyra et al. (2020) have reported the results of a study on the influence of plasma spray parameters especially electrical power as a variable on the mechanical properties of Al_2O_3 + 13 wt.% TiO_2 ceramic coatings. Higher degree of melting was associated with increased electrical power which increased the degree of cohesiveness in the coatings.
2. Vijay et.al (2007) have reported the significant influence spray coating parameters have on alumina-13 wt.% titania composite coatings synthesised by APS methodology, the focus being on deposition efficiency evaluated in terms of structural phases and microstructure. All parameters that are used in the APS coating system processing were studied and reportedly variations in them were said to bring about strong influence in the coating characteristics which included deposition efficiency, micro hardness, wear rates and the most influencing variable was identified as the input power.
3. C Arpagaus et al. (2019) have reported the importance of spray drying as a process methodology which is very efficient, simple and highly applicable for production of cutting-edge materials used in engineering, bio-technology, medicinal and energy sectors. Resulting in spherical shaped agglomerated powders, regardless of the starting powder morphology and size especially in nano dimensions, the paper included the various steps involved in the spray drying processing technique and specific applications in these areas.
4. Bingbing Fan et al (2017) have reported the synthesis and crystallization behavior of yttria partially stabilized zirconia nano powder by microwave pyrolysis process. Zirconium oxychloride octahydrate and yttrium nitrate hexahydrate were used as a starting material. The chemicals were mixed in distilled water, ammonia solution was added. The solution was stirred, filtered, washed, dried and kept in a microwave chamber at a suitable time and temperature. The nano powder thus obtained was characterized for microstructure, elemental composition and phase composition by Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS), Transmission electron microscope (TEM) and X- ray Diffraction (XRD). Comparison of structural phase with conventional pyrolysis was found. Powders were highly dispersive with average particle size of ~23 nm.
5. Yang Gao et. al. (2016) has described the results pertaining to feedstock of non-calcined yttria stabilized zirconia agglomerated powder in conventional APS and VLPPS deposition methodology. While the spray parameters affect the coating microstructure,

they are also influenced by the synthesis process of the agglomerated feedstock. The grains solidification mechanism of the powder particles and the resulting microstructural features were used to suggest that either fully nano-sized or bimodal equi-axed nano structures were formed in one or two stages during their flight through the APS system. Microstructural investigations were carried out on as-sprayed coatings and after long duration heat treatment at >1300℃ as well.

6. Yan Zhao and Yang Gao (2015) have reported their findings on spray dried Yttria stabilized zirconia (YSZ) powders which were coated by using APS coatings at two different current settings. They were compared with coatings processed under same conditions but by using commercial powders of same composition prepared by sintering. Micro- and crystal-structural analysis of the powders and nano structured coatings revealed the conditions under which the nano grains were retained better with associated changes or compromises that occurred in coating characteristics (porosity percentages and grain size variations). Results obtained from thermal conductivity studies performed on the one-dimensional steady state heat flow model in a furnace were also included.
7. Morteza Hajizadeh-Oghaz et al. (2015**)** have reported the results from synthesis of nano sized powder particles of MgO-stabilized ZrO_2 by Pechini Method. They employed statistical (Taguchi) method to study the influence of constituents used in the synthesis, molar ratios, and processing temperatures etc. on grain dimensions and homogeneity in dispersion that also allowed determination of optimum processing condition. The synthesized material analysis was performed by employing TGA, DTA, XRD, FESEM, TEM and Raman spectroscopy was also determined. The four influential factors were determined to be (a) citric acid to ethylene glycol mole ratio (b) citric acid to transition metal mole ratio (c) calcination temperature and (d) time.
8. Morteza Hajizadeh-Oghaz et al. (2014) have reported their findings on large scale synthesis of 8YSZ powders by Pechini method which resulted in >99.0 pure, near spherical powders with tetragonal crystalline structure. Among the chemicals used in synthesis citric acid and ethylene glycol were used as chelating agent and dispersant respectively. Suitable multiplications methods were engaged to upscale the yield from lab scale quantities (1 gram) to larger scale (30 grams).
9. Mohammad Reza Loghman-Estarki et al. (2013) reported the findings from their experiments conducted to synthesize scandium oxide and yttrium oxide zirconia co-doped nano powder synthesis by sol-gel method. The different types of spray dried suspensions were converted into plasma sprayable powders which were plasma spray coated. The

resulting coating microstructures were co-related with the feed stock powder morphologies, with focus on thermal insulation properties as well. The synthesis also attempted to increase the flowability of the powders obtained via the spray drying process. Plasma sprayable powders with low flow and densities negatively affected the coatings characteristics and so did the porosity of the nano YSZ granules themselves.

10. Yi Zeng et al. (2002) have reported the microstructures of nanostructured zirconia coating employed by using powders that were chemically synthesized and plasma spray coated. Characterized by a bi-modal structure, the coating comprised of poor consolidation of nano structure yet with micro hardness equivalent to sintered zirconia ceramic and micron sized grains overlying them. Difference in the thickness of the coating was due to presence of porosity and the dual structure formation, that is the poor and the other overlapping splat structure were comprised of with nano-sized and micron-sized particles. Presence of significant porosity was recognized as the major deterrent in the accuracy of hardness analysis which also was projected to affect the coating quality. Nano-indentation methods were suggested to be used for precision in micro hardness measurements.
11. X Q Cao et al. (2000) has demonstrated the usefulness of spray drying process for synthesis of flowing/ dry powders which is suitable for preparation of spray coatings comprised of materials compositions suitable for TBC applications. 3YSZ added with varying (0 to 6) percentages of alumina were spray dried and to study the highly relevant characteristics of spray dried powders being grain morphology and density. Binders and dispersants used in the process influence the rheological properties of the suspension.
12. Stanley J (1989) has conducted a review and reported the usefulness of spray-drying process to produce free flowing powder possessing constant bulk density obtained by granulating slurry loaded with the powder being spray dried. The review included a discussion on the influencing parameters such as slurry rheology, binder properties and spray drying technique itself.
13. S J Bull (1999) has reported the importance of using scratch test to assess the abrasive wear resistance of materials. A general practice is to provide a linear co relation of a hardness of the material with its wear resistance as an approximation which means harder the material harder the wear resistance, without considering adhesion of the coating. However the author reports significant variation in this methodology especially when thin and hard coatings are studied. The paper also cautions against using this test alone to obtain a quantitative estimate of wear rate without additional evaluation for specific cases.

14. J. Li &W. Beres (2007) has reported the scratch test where in a diamond stylus is made to move over the coated surface by providing a suitably increasing force moving over the surface of a sample to reach a critical stage when the coating fails. This force provides a good assessment of the adhesion quality of the coating with substrate. The test may be used on coatings and underlying substrates with a goal to evaluate their strength and adhesion quality with importance given to failure mechanisms and factors those influence them and Finite element models (FEM) to support the discussion.

3. PROBLEM IDENTIFICATION & STATEMENT

The research problems considered for this research work were the following

1. Synthesis of plasma sprayable powders from nano ceramic powder.
2. Fabrication of plasma sprayed ceramic coatings with nano-grained microstructure.
3. Synthesis of large scale (~100 grams) nano powders in lab scale.
4. Process control in spray drying and plasma spray coating nano powders.
5. Nano coatings to suit intended applications.

4. RESEARCH OBJECTIVES

The research work proceeds with the following objectives that entailed four comprehensive aspects (Process development, Synthesis, Characterization and Application).

1. Process development of (a) micron sized plasma sprayable powders from nano ceramic powders (8YSZ & α-Al_2O_3) and (b) Plasma sprayed coatings from above powders on substrates pertaining to diesel engine component materials.
2. Synthesis of nano ceramic powders - Yttria Stabilized Zirconia (8YSZ).
3. Characterization of the developed powders & coatings.
4. Coatings application on diesel engine components to evaluate engine performance.

5. TOOLS AND METHODOLOGIES

The objectives were accomplished in the following stages of development and evaluation:

- Development of process methodology to obtain micron sized plasma sprayable powders from ceramic nano powders (commercial) by (a) manual-granulation & (b) spray drying.
- Synthesis of 8YSZ nano powders in the laboratory scale by sol gel technique.
- Development of process methodology to obtain few tens of microns thick coatings from the above plasma sprayable powders with nano-grained microstructure on substrates and diesel engine components by Atmospheric Plasma Spray (APS) system.
- Studies on powder morphology, coatings microstructure and compositions by Scanning Electron Microscopy (SEM) & Energy Dispersive Spectroscopy (EDS), Structural phase analysis of the powders and coatings by X-ray Diffractometry (XRD). Powder flowability was evaluated by using Hall flow meter and APS system itself.
- Assessment of coating quality via thermal fatigue (shock cycles) tests (gas flame focused on ceramic coatings at 500℃ or 900℃ and forced air cooling alternately) in laboratory fabricated thermal fatigue test rig.
- SEM analysis on the coatings surface and cross section metallographic specimen removed from coated and thermal fatigue tested specimen to assess coatings quality, adhesion, coating-substrate interface quality, thickness and microstructure.
- Thermal barrier test to determine the temperature drop across coating thickness when coated surface was maintained at high temperature (at steady state) and metal substrate temperature at the backside of the coated substrate was measured.
- Evaluation of mechanical properties of the developed coatings by performance of wear, Vickers micro hardness and scratch adhesion tests.
- 8YSZ coated piston head assembly & α-Al_2O_3 coated gudgeon pin on 5HP, 1500 RPM, 4-stroke single cylinder diesel engine & engine performance evaluation (100 hours run).

6. FLOW CHART

Figure 1 shows the flow chart of the research process methodology. Details are described thereafter.

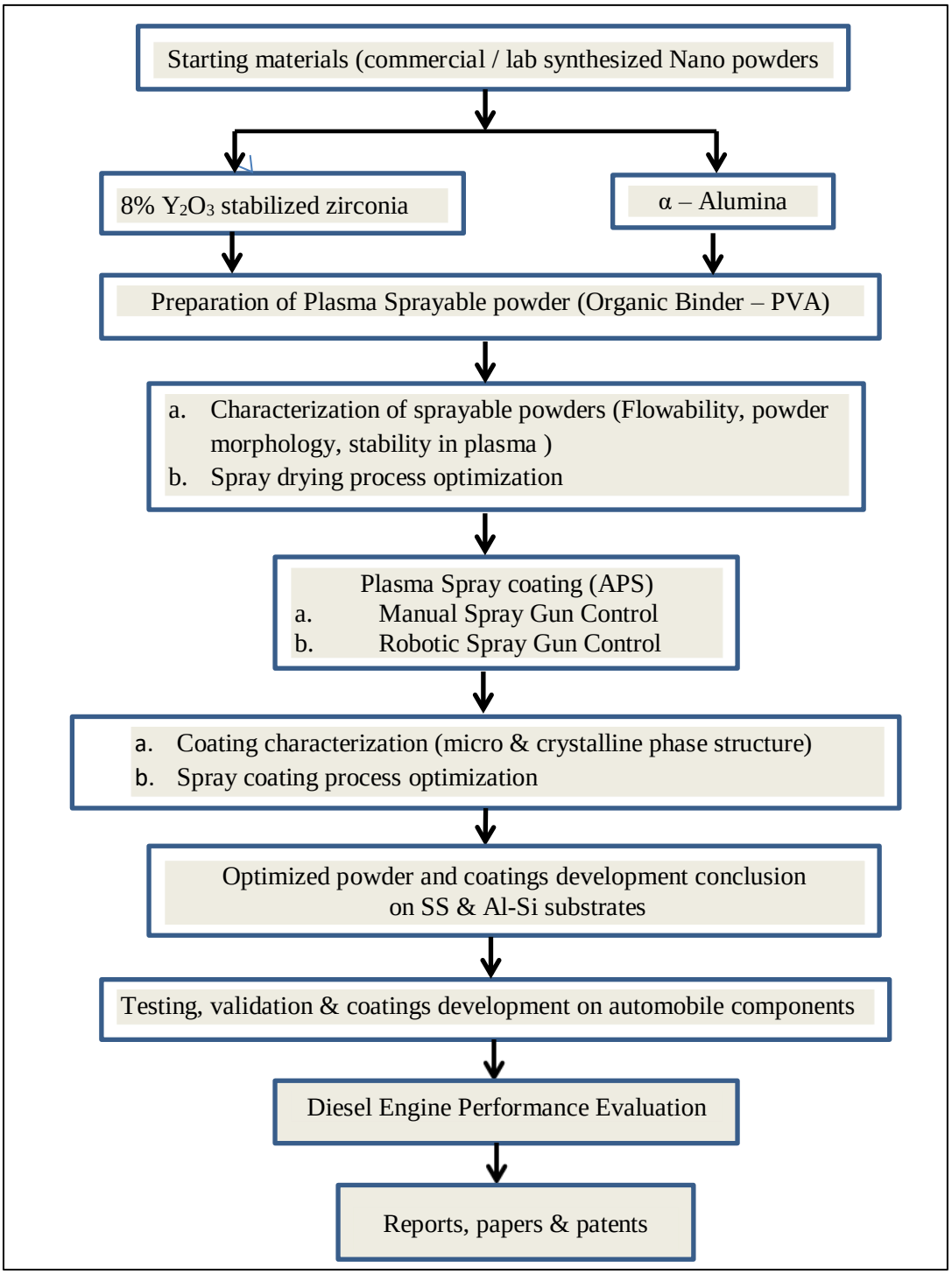

Starting materials (commercial / lab synthesized Nano powders
8% Y_2O_3 stabilized zirconia
α – Alumina
Preparation of Plasma Sprayable powder (Organic Binder – PVA)
a. Characterization of sprayable powders (Flowability, powder morphology, stability in plasma)
b. Spray drying process optimization
Plasma Spray coating (APS)
a. Manual Spray Gun Control
b. Robotic Spray Gun Control
a. Coating characterization (micro & crystalline phase structure)
b. Spray coating process optimization
Optimized powder and coatings development conclusion on SS & Al-Si substrates
Testing, validation & coatings development on automobile components
Diesel Engine Performance Evaluation
Reports, papers & patents

Figure 1 - Research Process Methodology Flow Chart

Commercially procured nano sized ceramic compositions (powders) or lab synthesized 8YSZ nano powders were used as starting raw materials to prepare plasma sprayable powders with the end goal to prepare 100 to 200 micrometer thick nano-

structured ceramic coatings. The powders, with grain sizes varying between 5 and 30 nm were reconstituted into spherical micro meter sized particles (typical size range of 45-90 microns) by manual method and by using Spray dryer for densification and free flowability. While an individual grain size of the densified nano-structured ceramic particles within the agglomerates was not more than 100 nm; the agglomerated powder particles constituting the nano particles were between 45 and 90 microns. The controlled agglomeration into larger particles with rounded morphology provided the free flowability of the powder after the spray drying densification process. The powder flowability was aimed to be at higher than 30 grams/sec with powder density >1.5g/cm^3. The reconstitution of nano powder into spherical micrometer sized plasma sprayable powder by using a suitable binder (PVA) was concluded by densification using an air circulating oven, controlled sieving and development of finer process control of spray drying process. The powders and coatings were characterized by Particle size analyzer, XRD, SEM and EDS. The flowability of the powders was evaluated by two methods: by using (a) Hall Flow Meter and (b) APS system itself. While the Hall Flow meter is a standard method to determine powder flowability, in the APS system flowability was measured by allowing the powder to flow through the spray gun with only the primary and secondary flow gases, followed by measuring the amount of powder flowing through the system per minute. This method also provided a fair estimation of the deposition efficiency. The ceramic coatings were produced by atmospheric plasma spray (APS) coating methodology followed by further optimization of plasma spray process parameters as well.

Keeping the end goal in view, the coatings were plasma spray coated on Al-Si (piston material) and SS (gudgeon pin material) substrates / plates. Once the process parameters were identified and optimized for obtaining the best coating characteristics, actual diesel engine components (piston and gudgeon pin) were plasma spray coated ensuring the retention of the irregular shapes and contours of the components.

After establishment of the coating process controls, the components were plasma spray coated and mounted on the diesel engine. The research work concluded with performance evaluation of the engine for 100 hours each (independent test for each component) followed by results analysis and evaluation of the coatings on gudgeon pin and piston head after the 100 hours endurance test.

7. RESEARCH WORK ACCOMPLISHED

Details of the materials processes and analysis methodologies are given below.

7.1 Process development of micron sized plasma sprayable powders

7.1.1 Manual granulation method

In order to plasma spray coat, the sprayable powder shouldn't be too fine or too coarse and should comprise of particle sizes between 30 and 75 microns (approximately). The nano powders (8YSZ or α-Al_2O_3) were reconstituted into plasma sprayable powders by following, the guidelines of published literature in the following manner.

a. Manual mixing of the nano powder with sufficient amount of polymers (organic binders). Appropriate binder content is significant to achieve strong physical bond between nano particles: excessive amount of binder leads to a closely packed powder with less scope for granulation with lower powder density and less quantity results in inadequate binding.
b. Uniformly mixed powder with binder sieved through 30 mesh sieves (~600 µm).
c. The sieved powders were oven dried at ~120°C for 2hrs to remove the moisture and sieved through ~170 mesh sieves (90 µm approximately). The powder particles that did not pass through this range of sieves were manually ground and the process was repeated. The sieved powders was once again passed through ~ 325 mesh sieve (~45 µm) to obtain the flowable powders that were retained at the top of the sieve. The powders, between 50 and 110µ were the plasma sprayable powders.
d. The extra fine powders that passed through the 45 µm sieve were remixed with binders again to undergo the same process as described above.

7.1.2 Spray Drying Method

Spray drying parameters were based on information obtained from the literature and determined mainly via experimentation followed by optimization techniques. Figure 2 shows a sketch of the major processes involved in the spray drying process.

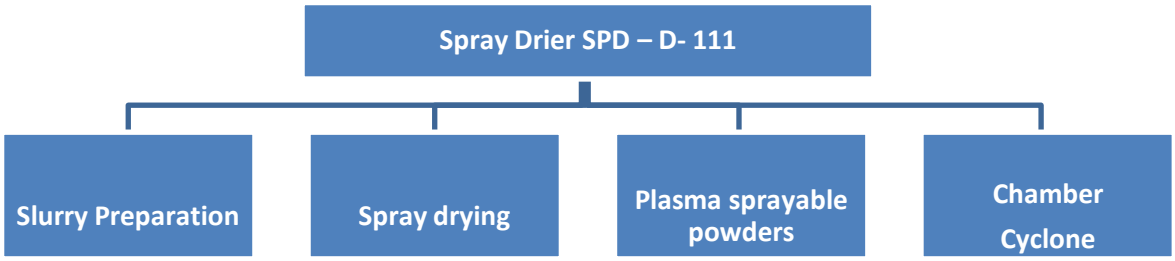


Figure 2 – Spray Drying Process

The main criteria employed for spray drying for obtaining maximum plasma sprayability during the coating process is the sprayed powder yield and flowability. The most important parameters that guide the spray drying process are (a) slurry characteristics and (b) spray drying conditions like inlet and outlet temperatures, slurry feed rate and pressure etc. A photograph of the spray dryer (with relevant parts identified) is shown in Figure 3.

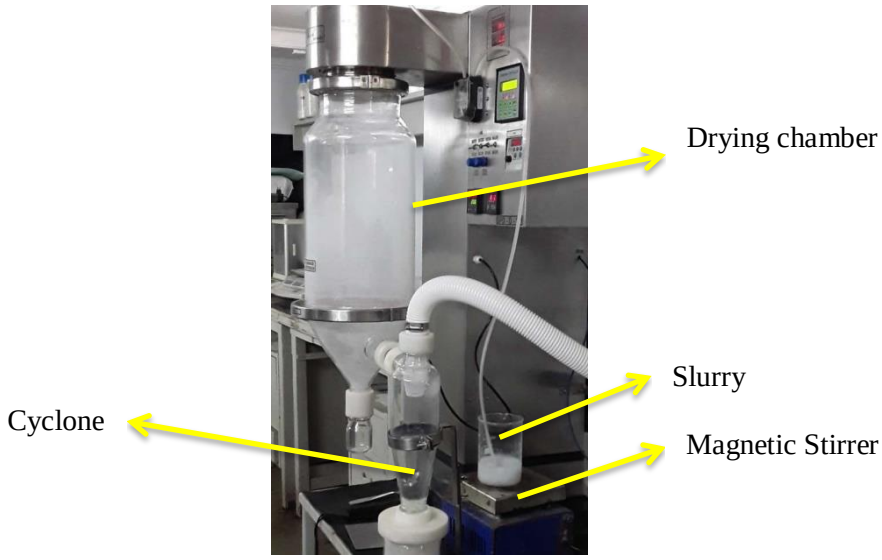


Figure 3 – Spray dryer

The process methodology and controls adopted for spray drying the nano powders are briefly described below.

(a) Synthetic polymer (PVA), used as the binder was weighed to an accuracy of 0.001 gram.

(b) Pre-fixed quantities binder (10 grams) and distilled water (100 ml) were magnetically stirred in a glass beaker at room temperature (~24℃), to completely dissolve the binder.

(c) 20 grams of nano 8YSZ (or nano α-Al_2O_3 as the case may be) were added to the solution, while magnetically stirring for an hour. This was the slurry, ready for spray drying.

(d) Meanwhile during above process, the spray dryer was switched on and the spray drying parameters were set. Stabilization of the inlet temperature (225℃) with estimated time (60 minutes) was carried out. After stabilization the process of spray drying was started.

(e) The slurry in the beaker was connected to spray drier equipment (placed on the in-built magnetic stirrer) through the connecting valves and tubes.

(f) While stirring was continued, the valve was fed in to the beaker to suck the solution through the feed pump valve (one way / two way) for spray drying in to the chamber (Coarse Particles), Cyclone 1 (Fine particles), Cyclone 2 (Very fine particles) and Cyclone 3 (Ultra-fine particles). The cyclone 3 was the scrubber (connected to blower).

(g) Spray drying process of powder takes around two hours to complete. The process was completed only after the system cooled down to room temperature (destabilization).

(h) Finally, the sprayable powders were collected from the chamber and the cyclone.

The challenges associated with this process are (a) raw material powder settling in beaker (b) slurry clogging the pipes (c) nozzle apertures clogging (d) inefficient stirring process due to slurry characteristics (e) slurry rheology management (f) insufficient output etc.

7.1.3. Synthesis of 8YSZ (yttria stabilized zirconia) nano powders

Nano powders of 8YSZ (yttria stabilized zirconia) were synthesized in the laboratory via sol-gel method. The process flow chart is shown in Figure 4.

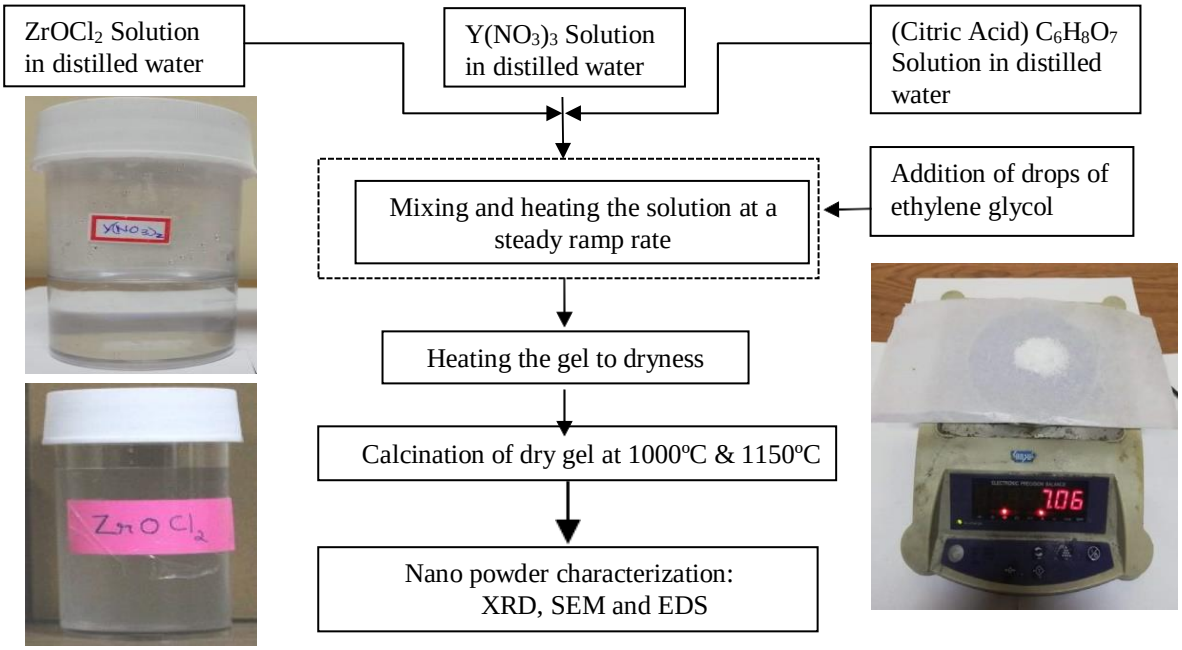

ZrOCl2 Solution in distilled water
Y(NO3)3 Solution in distilled water
(Citric Acid) C6H8O7 Solution in distilled water
Addition of drops of ethylene glycol
Mixing and heating the solution at a steady ramp rate
Heating the gel to dryness
Calcination of dry gel at 1000ºC & 1150ºC
Nano powder characterization: XRD, SEM and EDS

Figure 4 – Laboratory synthesis of 8YSZ (process flow chart)

Brief description of the process is given below.

(a) The two starting materials (precursor solutions) were zirconium oxy chloride ($ZrOCl_2$) solution and yttrium nitrate Y $(NO_3)_3$ solutions.

(b) The solutions were prepared from the starting raw materials in powder form and taken in the ratio of 97:3 by weight %. Solutions from the two powders were made separately by adding distilled water in the suitable proportions and mixed in a magnetic stirrer with continuous heating at a constant ramp rate. The solutions were mixed by stirring for 30 minutes to facilitate thorough mixing.

(c) Citric acid was added to this solution as a chelating agent (because the formation of multiple free ligands increases the chances of undesired products being formed). The solution was continued to be stirred under steady heating (up to ~350℃). When the solutions were being mixed, a few drops of ethylene glycol were added to facilitate

esterification reaction: this was done to remove the chlorine in the mixture by aiding the chlorine atoms to bond with hydrogen atoms and then escape as hydrochloric acid gas.

(d) As the synthesis progressed, the solution became denser followed by gel formation. The gel was heated until the moisture was visibly reduced.

(e) The dried gel was calcined at discrete temperatures from 800℃ up to 1150℃, such that t-ZrO_2 phase was formed without significant grain growth that exceeded the planned nano sized grain formation (particles exceeding 50 nanometers were not preferred).

(f) The sol gel developed powder also was spray dried in small quantity (~50 grams) and was subjected to spray drying to assess if it could be converted into plasma sprayable powder.

7.1.4 Evaluation of the flowability of spray dried powder: the flowability test

The flowability of the plasma sprayable powders was evaluated qualitatively by allowing the powder to flow through the plasma spray gun with only the flow gases and measuring the amount of powder flowing through the system per minute. This also allowed the estimation of the deposition efficiency. Hall Flow Meter was used to quantitatively determine the flowability of the plasma sprayable powders. The time taken by a fixed quantity of the lab developed powders to flow through the Hall tube was the measure of flowability. Figure 5 shows photographs of (a) the Hall Flow meter and (b) the flowability test in progress.

Figure. 5 - Photographs of (a) the Hall Flow meter and (b) the flowability test in progress.

The manually granulated and spray dried powders were tested for flowability. The powders collected in the chamber were determined to be free flowing and most suited for plasma spray coating, whereas the powders made from cyclone were not free flowing. Favourable results were also derived from the manually sieved powders in the lab. However considering the laborious process of manual powder preparation, a more efficient and faster process of

using a spray dryer (chamber) alone was adopted for all the further plasma sprayable powder processing.

7.1.5. Plasma sprayed coatings

The laboratory developed plasma sprayable (spray dried) powders were used to deposit nano-structured coatings: initially on (a) substrates & subsequently after establishment of best plasma spray coating parameters on (b) pre-identified diesel engine components. APS coating systems with different configurations (manual, robotic controlled, high & low power spray guns) were used to spray coat the powder. APS was used to spray coat the synthesized plasma sprayable powders from nano powders (8YSZ & α-Al_2O_3) on Al-Si alloy and stainless steel substrates. The substrates were chosen based on application envisaged: i.e. Al-Si alloy for piston and stainless steel for gudgeon pin applications.

50-75 µm thick bond coats were plasma spray coated prior to spraying of the top coats. Two types of bond coats were used: (a) Nickel Aluminide (Ni-Al)(METCO 450 NS) and (b) NiCrAlY (AMDRY 962). Figure 6 shows a photograph of the APS system used (kind courtesy NFTDC, Hyderabad). The robot controlled spray system is particularly useful where precision in coatings deposition is required.

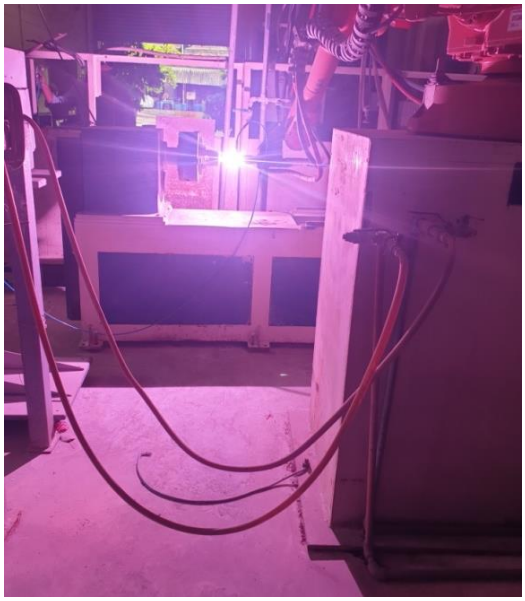
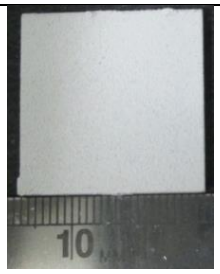


Figure 6 - APS with robotic controlled spray gun (facility @NFTDC, Hyderabad)

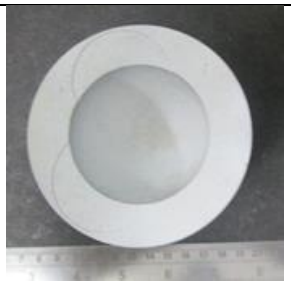
The optimization of spray parameters used in the preparation of the bond coat and the top coat were carried out at NAL, Bangalore, Spray Met Technologies, Bangalore, Bharathiyar University, Coimbatore, and NFTDC, Hyderabad. It has been reported that the coatings quality of plasma sprayed nano coatings can be increased by optimization of the critical Plasma Spray Parameters (CPSP) which is a function of current, voltage, and primary gas

feed rate and the spray distance. Photographs of nano ceramic coated substrates and engine components obtained with optimized CPSP are shown in Figure 7.

SS/α-Al_2O_3


Al-Si/8YSZ

Gudgeon pin


Piston

Coated pin & piston: ready to be mounted on engine

Figure 7– nano ceramic coated substrates and engine components

7.1.6 Optimized plasma spray coating parameters

Table 1 gives the optimized plasma spray coating parameters found suitable fabrication of coatings with nano grained microstructure on substrates and engine components.

Table 1 – Plasma spray coating parameters

Parameters	Bond coat (NiCrAlY)	Ceramic Top Coat (optimised)	
		8YSZ	α-Al_2O_3
Argon (1/min)	32	44	46
Hydrogen (1/min)	12	10	12
Current (A)	200	390	380
Voltage (V)	70	75	75
Nozzle /Electrode (mm)	5	5	5
Injector Diameter (mm)	1.3	1.6	1.5
Injector angle (Degrees)	90	90	90
Injector Distance (mm)	5	5	5
Powder gas (l/min)	3.2	3.2	3.2
Powder Feed Rate (g/min)	32	35	35
Spray Distance (mm)	90	85	90
Substrate Air cooled	Yes	Yes	Yes
No of passes	30	100	80

7.1.7. Deposition Efficiency

Deposition efficiency is based on plasma spray parameters such as flow rate, feed rate, current, power, grain size and spray distance, plasma properties like enthalpy, velocity and temperature etc. In APS system, after loading the plasma sprayable powders in the hopper, plasma spray parameters and hence plasma characteristics were modified to get the desired coatings under the best plasma conditions. That means not just good quality coating was important: equally important were good flowability of the powder through the plasma and

maximum deposition rate (deposition efficiency) for minimum powder loss. The deposition efficiency of bond coat powder was ~95-100% (minimal loss of powders), whereas the deposition efficiencies of top coat nano powders were significantly low at only ~45-50%.

7.1.8. Characterization of powders and coatings:

Most of the coatings were characterized when they were coated on substrates, except when they were coated on engine components and the engine performance was evaluated.

- Morphology and microstructure of the synthesized powders and coated substrates by Scanning Electron Microscopy (SEM), Elemental composition of powders by Energy Dispersive Spectroscopy (EDS), Structural phase analysis of the powders, coated surface via X-ray Diffractometry (XRD).
- Thermal fatigue tests (at 500℃ and 900℃) in laboratory scale thermal fatigue test facility.
- Coating thickness measurement and interface characteristics assessment by cross section metallography and SEM.
- Temperature drop measurement across coating thickness by thermal barrier test.
- Wear test to evaluate the wear performance of coatings.
- Hardness test to evaluate the strength of coatings.
- Scratch adhesion test to study the coating adhesion characteristics.

7.1.9. Thermal fatigue (shock cycles) tests:

Thermal shock resistance is an essential factor in determining the life of a TBC. Thermal

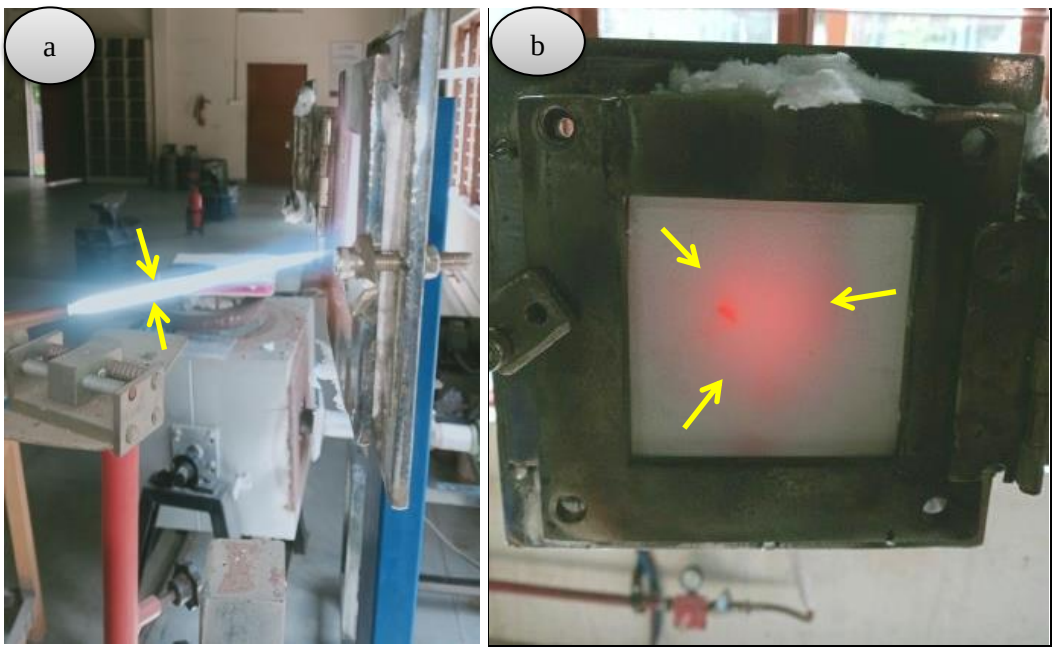


Figure 8 – Photographs of thermal fatigue cycle tests (a) Flame focused (arrows) on ceramic coating during the 1 minute heat-cool cycle and (b) Ceramic coating (arrows) after removal of the flame after completion of 1 minute heat cycle.

fatigue (shock) resistance tests were carried out with oxyacetylene gas flame focused on the TBC surfaces at maximum possible temperatures (to prevent melting or oxidation of substrates) followed by fan air quenching. 1- minute heat and 1- minute cool cycle was carried out which induced a thermal strain in the TBC system. The test on SS/nano 8YSZ was carried out for 500 thermal shock cycles at 900ºC and on Al-Si/nano 8YSZ for 500 thermal shock cycles at 500℃, due to the low melting temperature of Al-Si alloy. A non-contact Infra-red thermometer (IR gun) was used to measure the temperature on ceramic coating surface where gas flame was focused. Photographs pertaining to the tests are shown in Figure 8. The specimen was considered as failed if any coating peeled off or the test was stopped when a maximum of 500 fatigue cycles were attained.

7.1.10 Thermal barrier Test –Electrical Heating source

Thermal barrier effects of a TBC depend on many parameters: top coat and bond coat material, coating thickness, coating microstructure etc. The thermal barrier test arrangement, used to determine the thermal barrier effect of a TBC (ΔT) across the coating thickness by using an electrical heating source is shown in figure 9.

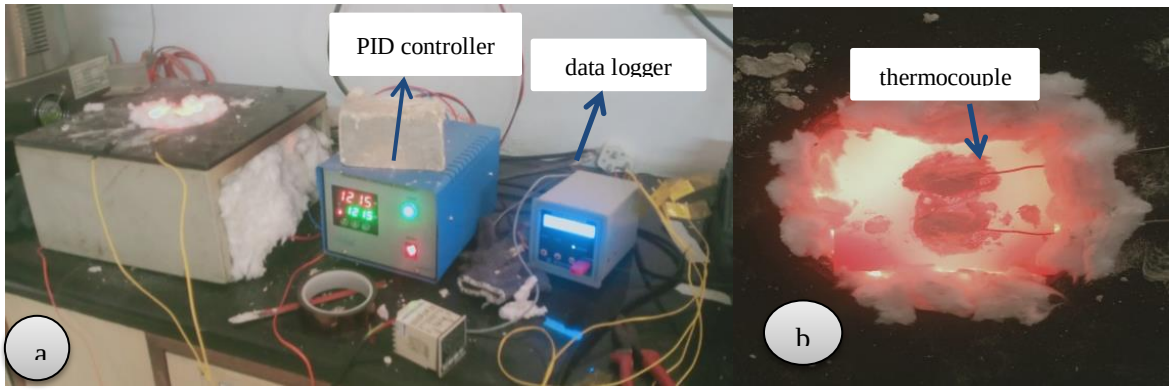


Figure 9 – Photographs of thermal barrier tests (a) set up and (b) Specimen mounted in electrical heating arrangement (thermocouples shown on back/metal side)

The ceramic coated surface was exposed to a temperature controlled heated surface and it was closely packed at the sides with thermally insulating glass wool so that heat would not radiate from the sides to the metal side. The temperature drop was measured across the thickness of the ceramic coating on the metal side. That is, the coated surface (hot) temperature (T1) and relatively colder metal side temperature (T2) at the back of the specimen were measured by using K-type thermocouples (cemented to the respective surfaces). The temperature drop across the coatings thickness (ΔT=T1-T2) was determined.

7.1.11 Diesel engine performance (with and without nano ceramic coated components)

To study the suitability of the developed nano-coatings for the intended applications

i.e. to improve fuel efficiency and also to protect against thermal damage and wear, the coatings were applied on actual engine components of a single cylinder 5HP engine. Heat resistant nano 8% Y_2O_3 - ZrO_2TBC for the piston and wear resistant nano α-Al_2O_3 coating for gudgeon pin were applied. The engine test facility consisted of four-stroke single cylinder, water-cooled 5HP (3.7285kW) diesel engine with DC Motor / Generator and a resistance load bank of 3.75 kW. The resistance load bank aids to load the engine to full capacity through which the damages to components due to thermal and mechanical loading can be assessed. DC motor/ generator aids the motoring test through which mechanical wear can be analyzed and characteristics curves obtained. Figure 10 shows the diesel engine facility used to evaluate the coated components and thereby the coatings. The details are as the following.

a) Nano Thermal Barrier Coatings (TBCs): Piston Crown

Low Heat Rejection (LHR) concept in the diesel engine was evaluated by thermally

Figure 10 - 5 HP Single Cylinder Diesel Engine Test Rig

insulating the piston crown, a combustion chamber component. 8% Y_2O_3 - ZrO_2 coatings with nano grained microstructure was applied on the piston crown and the engine was run for 100 hours and the performance was compared with that of OEM engine.

b) Wear resistant Nano Coatings (WRCs): Gudgeon pin

To evaluate the coating quality at maximum load, the diesel engine was mounted with gudgeon pin coated with α-Al_2O_3 coatings (with nano grained microstructure) and the engine was run for 100 hours. The state of the coating on the gudgeon pin was assessed after the engine performance test was completed.

Figure 11 shows a photograph of the coated engine components (gudgeon pin and piston).

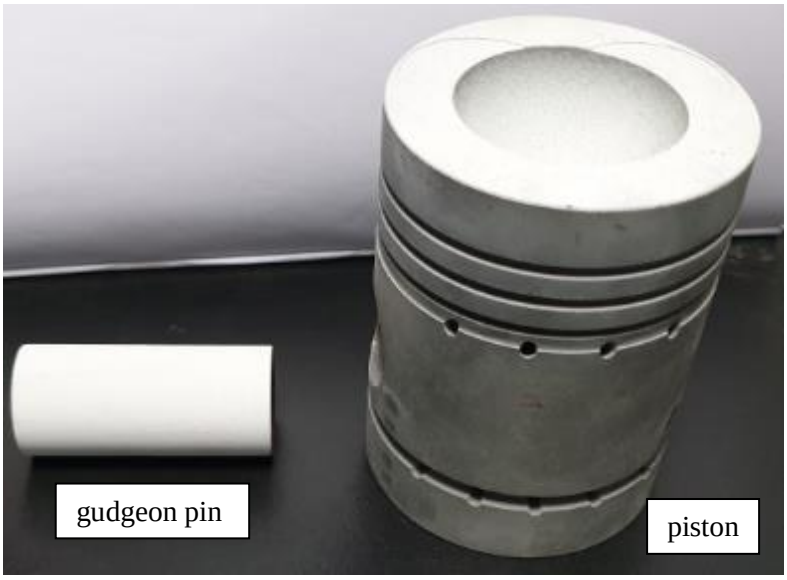


Figure 11 - Photographs of nano ceramic coated Gudgeon pin (NiCrAlY/ α – Al_2O_3) and Piston (NiCrAlY/ 8YSZ): ready to be mounted on engine

8. RESULTS AND DISCUSSION

8.1: nano 8YSZ and nano α-Al_2O_3 (commercial): Findings from these powders when converted into plasma sprayable powders and coatings thereafter are given below.

8.1.1 Commercial raw material powder morphology by SEM:

The particle morphologies of the commercial 8YSZ and α-Al_2O_3 raw material nano powders, studied under SEM are shown in Figure 12 (a and b). The average particles sizes were ~50nm. The particles were severely agglomerated and the presence of nano powders were detected after careful observation of the microstructure at >100kX magnification in the SEM. Resolution would be much better when Transmission Electron Microscope (TEM) is used.

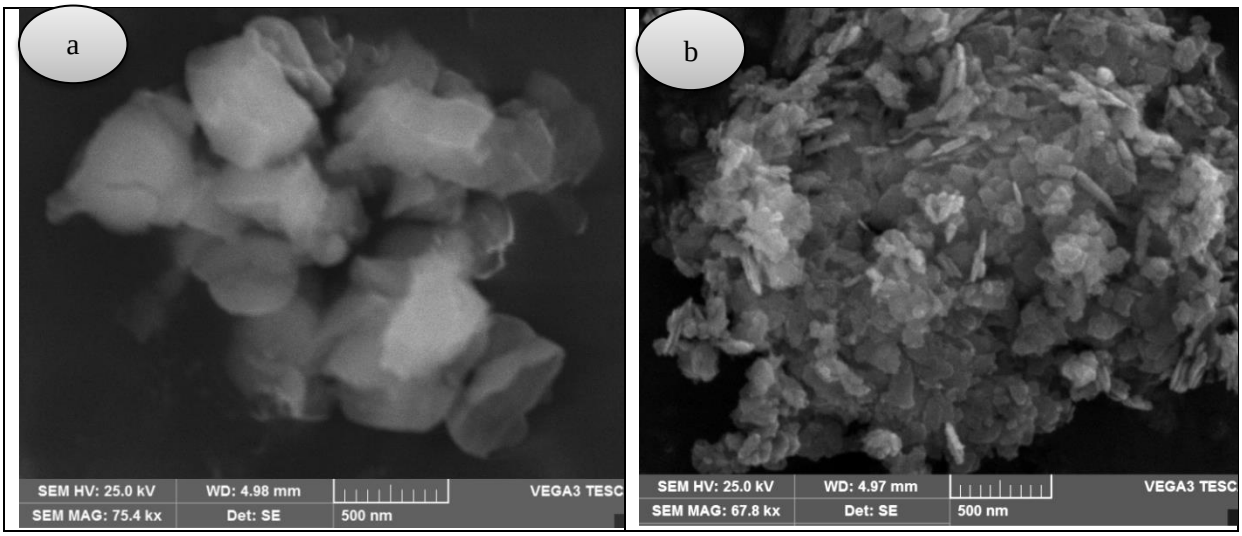
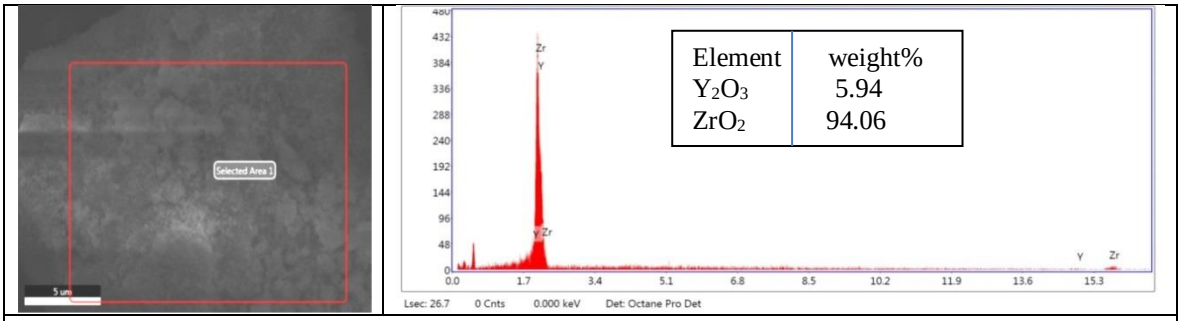


Figure 12 – SEM micrographs of commercial (a) 8YSZ & (b) α-Al_2O_3 raw nano powders

8.1.2: Chemical composition analysis of commercial 8YSZ nano powder by EDS:

Fig 13 shows the chemical analysis of commercial 8YSZ nano powders determined via EDS. Y, Zr and O peaks were identified via qualitative analysis. Quantitative elemental analysis followed by combining the elements into oxides in stoichiometric ratio gave the oxide contents as ~6%Y_2O_3 and ~94% ZrO_2 respectively. Similarly the chemical analysis of α-Al_2O_3 confirmed the raw material to be only Al and O, with negligible impurities and therefore most likely to be >99.0% Al_2O_3.



Element	weight%
Y_2O_3	5.94
ZrO_2	94.06

Figure 13 – SEM image, EDS Pattern and chemical composition of 8YSZ nano powders (commercial)

8.1.3: Structural phase analysis of commercial 8YSZ nano powder by XRD

XRD confirmed ~85% tetragonal 8YSZ (t-ZrO_2) phase of the commercially procured nano 8YSZ powder, the balance was ~15% monoclinic zirconia (m-ZrO_2) phase (Figure 14). The t-ZrO_2 phase was represented by the three major peaks: at 2θ = 30.2093, 50.2960 and 59.8233, while the two {111} family of planes on either side of the (111) peak of t-ZrO_2 at 2θ = 30.2093 were the minor (100%) m-ZrO_2 peaks.

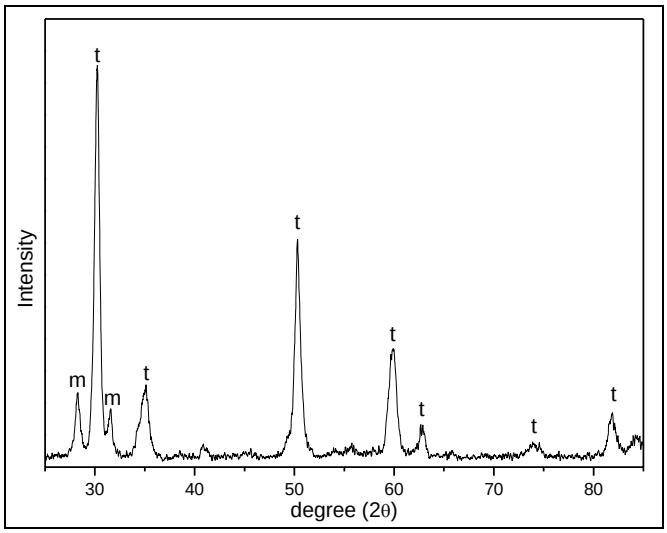


Figure 14 - XRD Pattern of 8YSZ Nano Powder (commercial):
(m and t represent monoclinic and tetragonal ZrO_2 respectively)

XRD pattern of commercial nano alumina powder (diffractogram not shown here) confirmed the major phase to be corundum (α-Al_2O_3). Absence of any un-identified major peak confirmed the phase to be >99.0 % purity (<1.0% minor unidentified peaks).

8.2: Laboratory synthesized 8YSZ nano powders:

The 8YSZ powders, synthesized in the laboratory by employing Pechini process [1] were characterized for morphology and chemical composition by SEM& EDS and structural phase by XRD. The findings are described below.

8.2.1: Lab Synthesized 8YSZ nano powder morphology by SEM

The powder morphology and grain size measurements of all powders (calcined gels, ground in pestle and mortar) were carried out in SEM. All the powder samples were analyzed at near identical conditions (working distance 4.9 to 5.1 mm, magnification ~320 kX to 323kX, mounting method etc.). The powder morphologies of all particles were similar, angular, slightly elongated and not totally rounded. In contrast, there was significant variation in the particle sizes. The nano powder particles (commercial) were closer to the averarge size of ~50nm while the lab-syntheized nano powders were in the size range of ~10-90 nanometers: however these sizes fell within the range of optimum grain sizes (<100 nm) desired for obtaining nanograined microstructure and thereby were well-suited for conversion into

plasma sprayable powders as well. As described previously, SEM image quality at such high magnifications are compromised. Typical SEM micrographs are shown in Figure 15 (a & b).

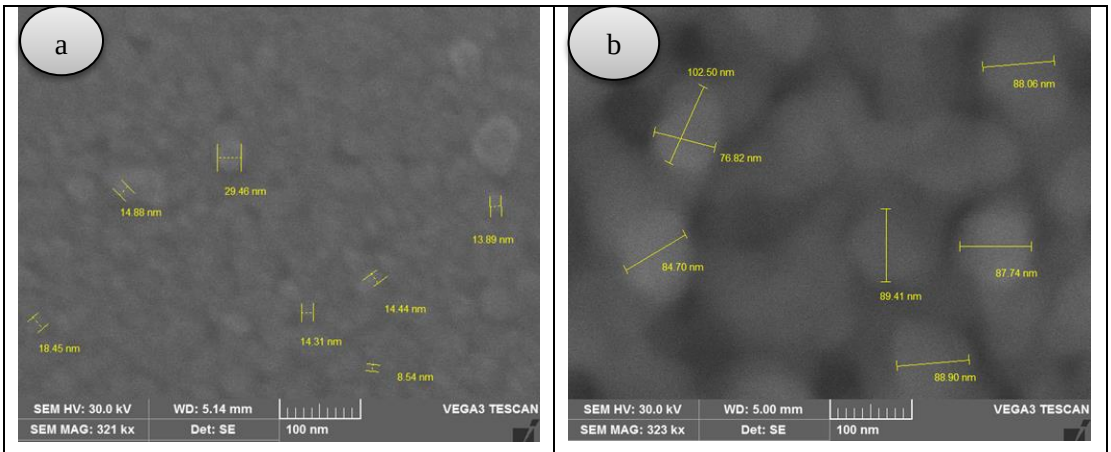
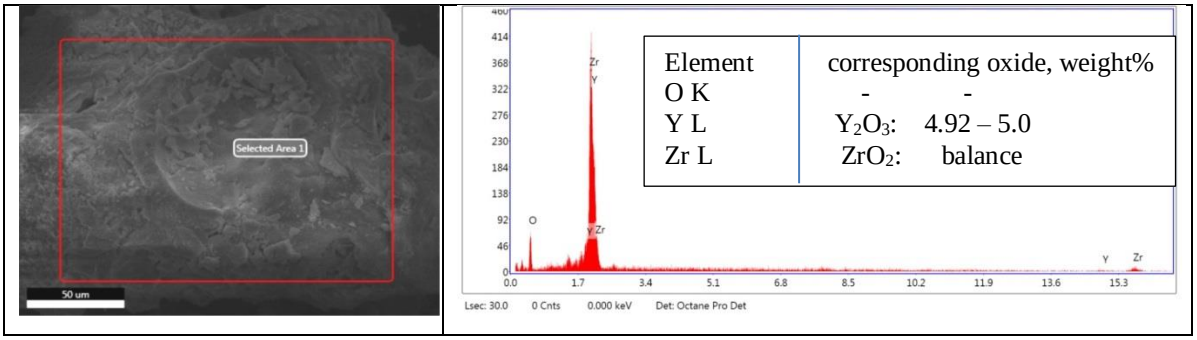


Figure 15 - SEM Micrographs of lab synthesized 8YSZ nano powder

8.2.2: Chemical composition analysis of lab synthesized 8YSZ nano powder by EDS

Chemical composition analysis (qualitative) of the lab synthesized 8YSZ nano powder by



Element	corresponding oxide, weight%
O K	- -
Y L	Y_2O_3: 4.92 – 5.0
Zr L	ZrO_2: balance

Figure 16 - EDS Pattern and Elemental composition of 8YSZ nano powders (lab synthesized)

EDS is shown in Figure 16 which showed presence of Zr, Y and O (no impurity). The likely phase was 5% Y_2O_3-ZrO_2: the t-ZrO_2 phase was confirmed by XRD.

8.2.3: Structural phase analysis of lab synthesized 8YSZ nano powder by XRD

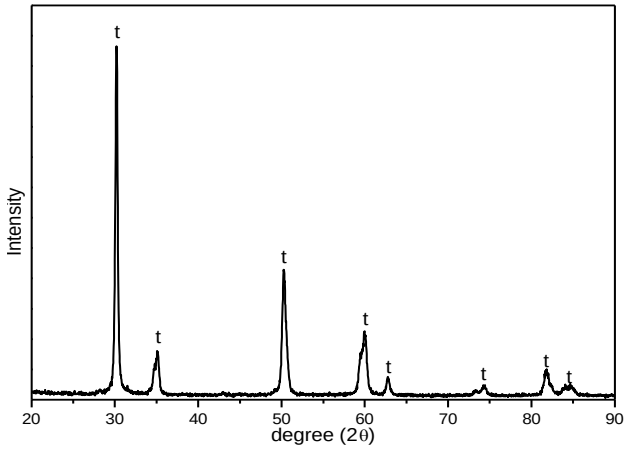


Figure 17 - XRD pattern of lab synthesized 8YSZ Nano powder

Figure 17 shows the XRD Pattern of lab synthesized 8YSZ nano powder calcined at 1000℃. The structural phase of the powders was confirmed to be 100% t-ZrO_2. Integrating the qualitative EDS and XRD pattern on lab synthesized nano powder, it could be concluded that highly pure yttria stabilized zirconia nano powders could be synthesized by systematically by following the sol-gel method of synthesis. No monoclinic ZrO_2 peak was observed unlike in the case of commercial nano 8YSZ powder (Figure 14).

8.3: Plasma sprayable powders

8.3.1: Yield and flowability of plasma sprayable powders – 8YSZ

Table 2 shows the yield and flowability characteristics of the plasma sprayable powders synthesized by (a) manual and (b) spray drying methods of agglomeration. The powder characteristics for both types of powders were highly similar. Both were free flowing: however the spray dried powders synthesis was more efficient with higher yield and therefore considered to be the preferred method for plasma spray powder synthesis. Similar results were obtained for α-Al_2O_3 plasma spray powder as well. Trials were based on optimization of spray drying parameters, composition of binder, distilled water, PVA and raw material.

Table 2 - Yield and Flowability characteristics of 8YSZ Plasma Sprayable powders

Trials	Manual		Spray Dryer (chamber)	
	Yield (%)	Flowability (Grams/Minute)	Yield (%)	Flowability (Grams/Minute)
1	46	43.5	44	42.5
2	35	38.4	35	39.6
3	44	42.5	48	44.5
4	42.6	41.2	72.7	43.5
5	66	45	37.2	46
6	78	48	58.5	48

8.3.2: Plasma sprayable nano powder morphological studies of 8YSZ and α-Al_2O_3 by SEM

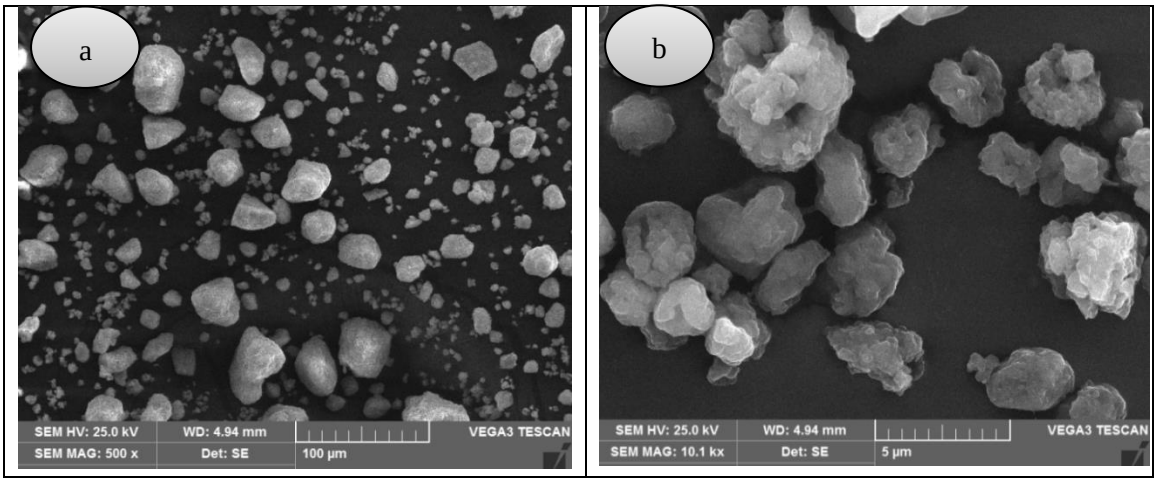


Figure 18 – SEM micrographs (a) 8YSZ and (b) α-Al_2O_3 - plasma sprayable nano powders

The particle morphologies of the two types of plasma sprayable powders, studied under the SEM is shown in Figure 18 (a and b). The agglomerated powder particles were irregular in shape and measured between 5 and 100 µm. Although SEM is not the ideal instrument to study the agglomerated powder morphology, and dry powder feed particle sizer is required for the same, SEM analysis does provide the basic information needed to support the understanding about the free flowability of the plasma sprayable powder.

8.4: Microstructural analysis via SEM on metallographic cross section removed from as sprayed coatings

The microstructures (SEM micrograph) of 8YSZ spray coated surface and α-Al_2O_3 spray coated surface (studied in cross section) are shown in figure 19 (a and b). The microstructure obtained at a magnification of 400 X (fig 19 a) shows the coating thickness of 8YSZ to be ~ 200 µm and that of α-Al_2O_3 coating to be ~ 130 µm (fig 19 b). Variations in the coating thicknesses are observed which depend upon the number of passes used for coating the particular specimen. The coating thickness build-up was up to 10 µm/pass of the spray gun over the substrate. Furthermore, while it was expected that both the powders would have similar plasma sprayed coating characteristics, the results suggest enhanced coating thickness development in 8YSZ, likely due to higher densities of 8YSZ compared to α-Al_2O_3.

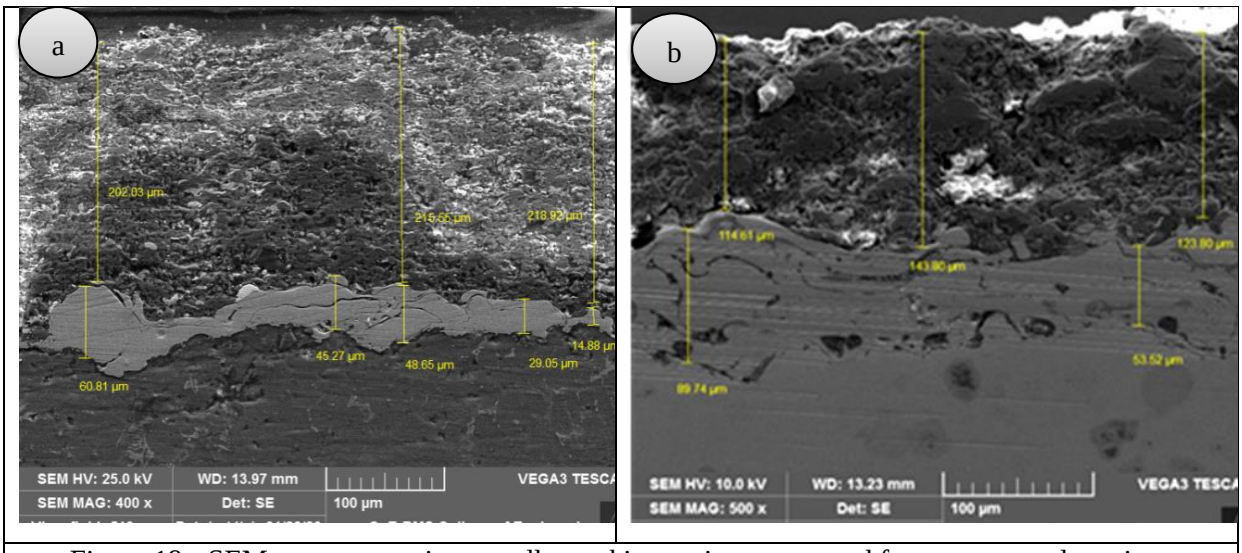


Figure 19 - SEM on cross section metallographic specimen removed from as sprayed coatings (a) 8YSZ and (b) α-Al_2O_3

8.5: Materials Analysis on 8YSZ TBCs - thermal fatigue tests

The 8YSZ TBC surfaces after completion of 500 thermal fatigue tests were analyzed for signs of deterioration, if any. The SS/8YSZ TBC withstood 500 thermal shock cycles / heat quench between 900℃ and ambient while the Al-Si/8YSZ TBC withstood 500 thermal fatigue cycles between 500℃ and ambient without failure. Results are described below.

8.5.1: Microstructural analysis of 8YSZ TBC surfaces by SEM:

Figure 20 & 21 shows the microstructures of the coated surfaces (before & after thermal fatigue tests).

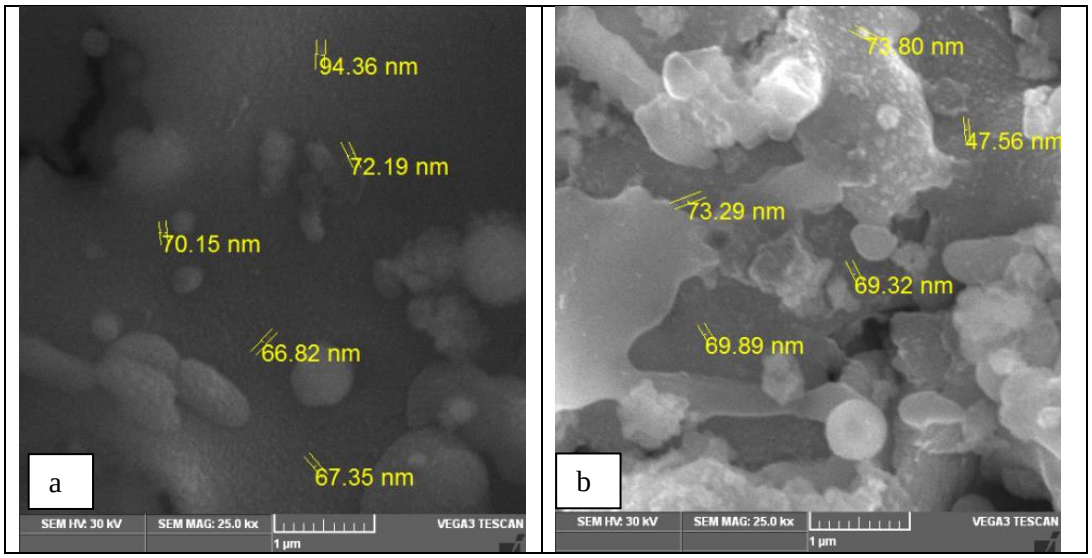


Figure 20 - SEM micrographs of 8YSZ TBC as spray coated surfaces on (a) SS & (b) Al-Si

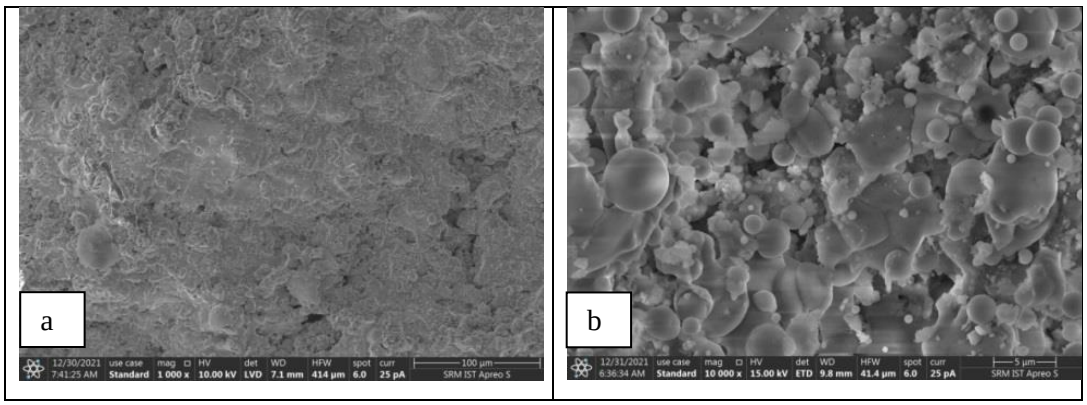


Figure 21 - SEM micrographs of 8YSZ TBC surfaces after thermal fatigue test on (a) SS & (b) Al-Si

Detailed SEM analysis at high magnifications (25.0 kX) confirmed the average grain sizes to be (a) SS/8YSZ ~ 80 nm and (b) Al-Si/8YSZ ~ 60 nm respectively. Characterized by rounded grain morphology, no cracks, some porosity the coatings were devoid of defects. Detailed SEM analysis of thermal fatigue tested specimen at high magnifications did exhibit some exaggerated grain growth (~3 µm sized grains). However, the average grain sizes were found to be (a) SS/8YSZ ~ 90 nm and (b) Al-Si/8YSZ ~ 70 nm respectively, with maximum grain sizes to be ~ 0.5 µm.

8.5.2: Microstructural Analysis via SEM on metallographic cross section removed from 8YSZ TBCs after Thermal Fatigue tests

Figure 22 (a and b) shows the SEM micrographs of the thermal fatigue tested 8YSZ TBCs analyzed on polished metallographic cross sections. No significant damage (other than grain pull-outs) was observed on the coating thickness and microstructure.

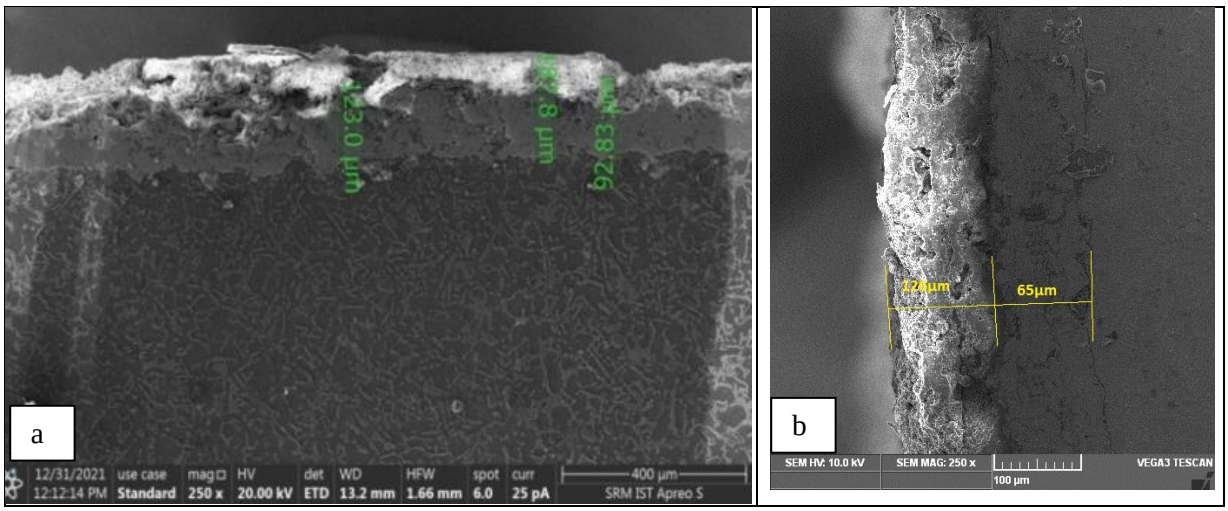


Figure 22 - SEM Micrographs of 8YSZ TBCs on (a) SS & (b) Al-Si after thermal fatigue tests

The 8YSZ coating thicknesses were found to be between 100 and 120µm on both the coatings (SS and Al-Si substrates) while the bond coat was ~65µm thick.

8.5.3: Structural phase of 8YSZ surfaces by XRD – as sprayed and after thermal fatigue test

Figure 23 shows the typical XRD patterns of nano 8YSZ TBCs on SS (a) as sprayed and (b) after thermal fatigue tests. It may be recalled that the starting raw powder (commercial 8YSZ) comprised of ~85% t-ZrO_2 (Figure 14). The 8YSZ coated surface exhibited a similar pattern, except the pattern was pre-dominantly t-ZrO_2 (>95%) while the m-ZrO_2 phase retention was reduced to <5% after completion of plasma spray coating process. That is, the plasma spray coating process further stabilized the t-ZrO_2 phase, as well as rendered it slightly glassy (noisy pattern) with splitting at higher diffraction angles. Thermal fatigue testing slightly destabilized the t-ZrO_2 phase to ~80% (Figure 23b), although the pattern became fairly more crystalline most likely due to the heat treatment during thermal cycling between 900℃ and ambient and the splitting of peaks disappeared. α-Al_2O_3 coated surface was 100% α-Al_2O_3 and the pattern depicted high amount of crystallinity (pattern not shown).

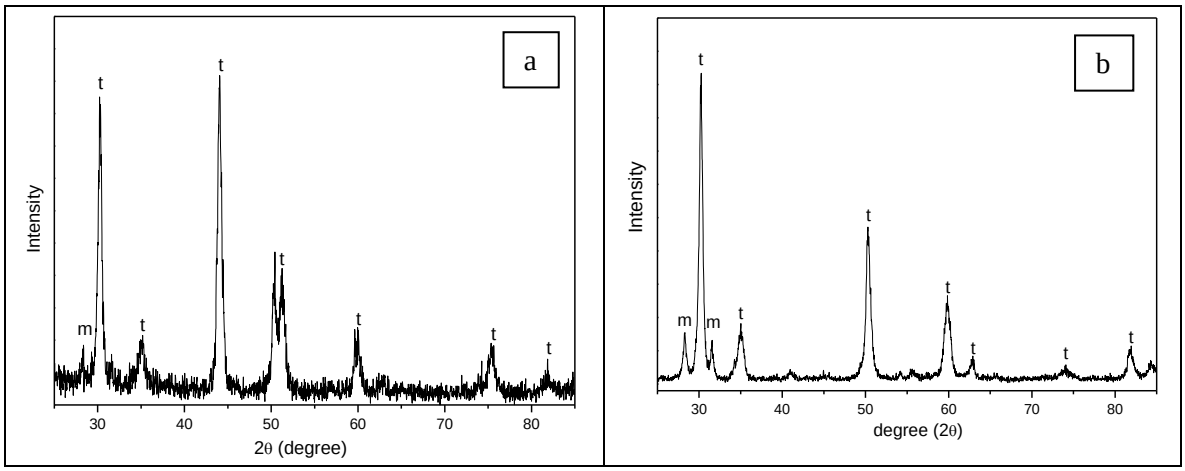


Figure 23 - XRD pattern of nano 8YSZ TBC (a) as sprayed and (b) after thermal fatigue test (900℃)

8.6: Wear test on nano α-Al_2O_3 coatings

Abrasive wear test on nano α-Al_2O_3 coatings confirmed its superior quality. This was revealed by the negligible wear (0.39% to 1.89%) it exhibited during scratch abrasion test at 5N and 20N loads. Wear percentage loss of α-Al_2O_3 coatings on the substrates (Al-Si and SS) although were varied but marginal: the variation is a function of the load and microstructure. The low wear characteristics confirmed the suitability of the nano alumina coatings for wear resistant applications. Table 3 and 4 shows the test settings, parameters set and the results.

Table 3 – Wear Test Parameters (settings)

Test parameters			Machine settings		
Expt. No.	Applied Load (N)	Sliding velocity (m/sec)	Sliding dia (mm)	R.P.M	Time (minutes)
1	5	1.5	40	717	11.1093
2	20	1.5	40	717	11.1093

Table 4 – Wear test reults

Load	Samples	Initial weight g	Final weight g	Wear loss (g)	Wear loss (%)
5 N	Al-Si/ α- Al_2O_3	0.514	0.512	0.002	0.39
	SS/ α- Al_2O_3	1.413	1.411	0.002	0.14
20 N	Al-Si/ α- Al_2O_3	0. 528	0.518	0.01	1.89
	SS/ α- Al_2O_3	1.401	1.386	0.015	1.07

Similar reports have been reported in the literature. Singh et. al has reported the superior sliding wear behavior of plasma sprayed nano structured alumina when compared with similarly fabricated micron structured alumina coatings. The superiority of the wear behavior of nano alumina coatings is attributed to the bi-modal microstructure, such as melted and un-melted α- Al_2O_3 regions complimented by presence of fine particle dispersion and milder deformation characteristics [2]. The wear loss values for the coatings at the lower load i.e. at 5N were as expected, lower than the values at 20N load as well. Further, the coatings on Al-Si substrates were notably higher i.e. 0.39% and 1.89% against the low 0.14% and 1.07% by coatings on SS substrates' at 5 and 20N load respectively. The wear resistance of the nano alumina coatings on SS substrates was slightly higher than those on Al-Si substrates. This could be because the adhesion characteristics of coatings on different types of substrates have since long been recognized to be influenced by a variety of factors such as (a) very high expansion mismatch (aluminium alloy and oxide ceramic), (b) residual stress generated during coating (c) substrate temperature during coating (d) oxidation etc. and a detailed study is required to attribute a precise mechanism for the slight improvement in the wear behavior of nano alumina coatings in SS substrates than on Al-Si substrates [3].

8.7: Hardness tests on the nano coatings

Table 5 shows the Vickers micro-hardness numbers (VHN), determined on the coatings in polished metallographic cross sections. The indents were dropped only on the coatings and not on the substrates. The tests were conducted at 50 grams load and 10 seconds dwell time.

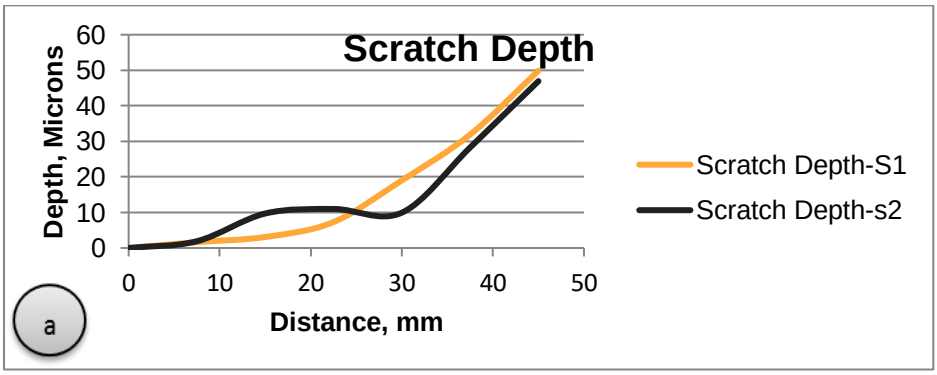
Table 5 – Hardness test results H.V at 0.05 Kgf, Unit: HV

Coatings	Trial 1	Trial 2	Trial 3	VHN (Average)
SS/8YSZ	978.4	1015.3	1008.1	1000.6
Al-Si/8YSZ	958.3	987.6	982.1	976.0
SS/α-Al_2O_3	1012.5	1004.9	1014.9	1010.7
Al-Si/α-Al_2O_3	988.6	994.2	993.1	991.9

The average VHN for 8YSZ on SS and Al-SI were 1005 HV and 976 respectively. The drop in the hardness values of coatings on Al-Si was most likely due to the small variations in the spray parameters. Similarly the average VHN for α-Al_2O_3 on SS was ~1010 and 992 on Al-Si. The slightly reduced value corroborated with the previous results of 8YSZ attributable to spray parameters.

8.8: Scratch tests on the nano coatings

The scratch test is a simple engineering test method, which is used to assess the adhesive bonding between coatings and substrates. The results obtained are influenced by various factors like coating thickness, coatings microstructure, substrate properties, dimensions of the substrate, bond strength and testing conditions such as scratch speed, load and indenter tip radius. The load can be fixed or gradually increased. This test was carried out on the nano grained coatings fabricated in this research work as well. The output was measured in terms of penetrating depth and frictional force. The test results are shown as graphical representations in Figure 24 (a and b) which comprise of (a) distance Vs scratch depth and (b) distance Vs scratch friction.



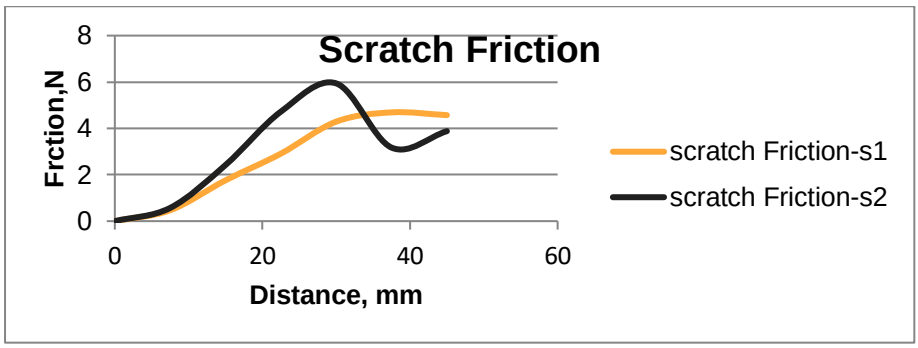


Figure 24 - Graphical Representations of scratch test results (a) Distance Vs Depth and (b) Distance Vs Friction

The load, at which the first crack appears is called lower critical load, which is a measurement of the cohesion strength of the coatings. The load, at which the total peeling off the coatings from the substrate occurs, is called the upper critical load, which is a measure of the adhesion strength of the coatings to the substrate. Even at constant load the applied pressure acting on the hard surface varied due to coating property. Once a tear occurred on the coating, further penetration was easier due to the ductile force that gave the higher frictional force. The friction and the depth may increase or decrease as a function of many parameters (coating characteristics and test conditions). Figure 24 (a) shows the plots of scratch distance vs. depth for the two coating systems studied. The depth value was constant initially and increased with increasing distance. During the initial stages, depth was minimal on both the samples due to micro-contact between the coating and the tip. In case of sample 1, the depth value was constant and increased gradually after 10 mm. But in sample 2, the depth value remained fairly constant up to 30mm, then gradually increased. This could be attributed to the material properties and coating characteristics.

Figure 24 (b) shows the plots of scratch distance vs. friction for the two specimens. It is inferred that friction value was increased with increasing the distance. During the starting stage, low friction was noticed on both the samples due to micro-contact between the substrate and the tip. In sample 1, the friction value becomes constant after 30 mm unlike in sample 2 where a sudden drop was noticed at same distance. These features may be attributed to the change in contact mode during test and spallation of the material from the sample.

The results in numerical values are shown in Tables 6 and 7 respectively. The results showed that and average depth of ~ 18.8 µ and average friction of ~ 3.11 N on SS/α-Al_2O_3 while it was 17.9 µ and ~ 3.45 N respectively on Al-Si/8YSZ. To summarise the results, the indenter did not penetrate the coating to more than 19 µ on an average which largely relates to the adhesion strength of the coatings on coating thicknesses up to 170 µ (~10 % of coating thickness).

In the figures, S1 pertains to SS/ α-Al_2O_3 and S2 pertains to Al-Si/8YSZ coated systems.

Table 6 – Scratch test results on SS/ α-Al_2O_3

Distance (mm)	Scratch Depth-s1 (microns)	Scratch Friction-s1 (Newton)
0	0	0
7.5	1.64	0.47
15	3.1	1.76
22.5	7.3	2.91
30	19.03	4.29
37.5	31.9	4.69
45	49.87	4.57

Table 7 – Scratch test on Al-Si/8YSZ

Distance (mm)	Scratch Depth-s2 (Micron)	Scratch Friction-s2 (Newton)
0	0	0
7.5	1.91	0.57
15	9.7	2.42
22.5	10.98	4.72
30	9.93	5.94
37.5	28.28	3.17
45	46.94	3.88

The findings reconfirmed the soundness of the coatings quality in terms of adhesion which in turn was related with the coating hardnesses (980 HV and 1010 HV). The significance of friction coefficient and wear resistance are linked with surface topography and: that is smoother surfaces generally provide low friction coefficient [4]. The average frictional resistance of 3.5 N and 3.15 N although did not signify a highly smooth surface as was expected from a nano structured coating. Friction resistance of <1N is known to be better suited [4]. The slightly high friction resistance value is most likely due to the uneven surfaces presented on the top most surface of the coating. Mild grinding is expected to highlight the nano surface microstructure which has been tried. The properties improved and the findings will be detailed in the thesis.

8.9: Performance Evaluation of baseline and modified engine

The 5 HP single cylinder diesel engine with nano 8YSZ coated piston and nano α-Al_2O_3 coated gudgeon pin was evaluated for performance and was compared with the performances of engine with baseline (uncoated components) engine.

Results are presented below.

8.9.1: Performance of engine mounted with nano 8YSZ coated piston

Figure 25 shows the results obtained after conducting the performance evaluation of the diesel engine mounted with the nano 8YSZ coated piston head (modified engine) and compared with the performance of baseline engine (engine with original un-coated piston) for a 100 hours of engine run time.

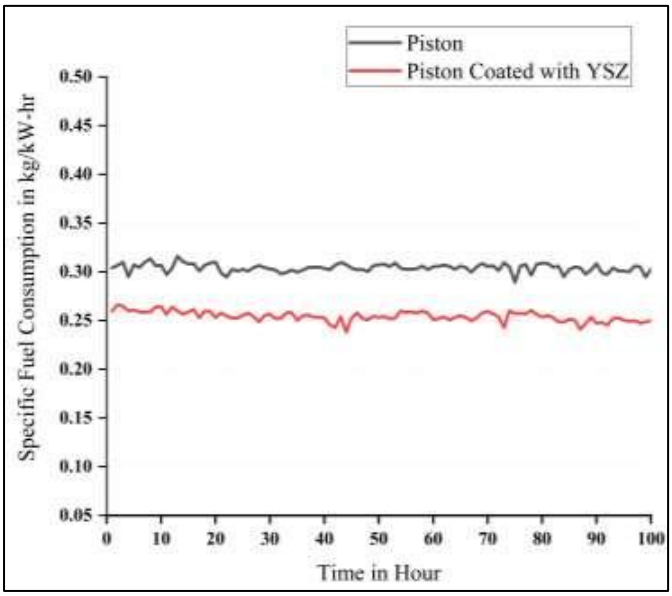


Figure 25 - Nano 8YSZ coated piston in diesel engine – SFC vs. time graph

Fuel consumption / performance of diesel engines with conventional 8YSZ TBCS (micron grained microstructure) have been highly varied (mostly 3% to 11% and occasionally up to 20% for high engine speeds) [5, 6, 7]. Significant reduction in the Specific fuel consumption SFC (22%) in the modified engine was the major finding and accomplishment.

The result strongly suggests the significant influence of nano 8YSZ coatings as TBCs to enhance the combustion within the engine. The significantly high performance (reduction in SFC), as observed in the present research work is expected because nano structured coatings have been found to be more strain tolerant than the conventional type of 8YSZ microstructure even when produced with APS system [8]. This is also due to the best thermal insulation provided by these coatings inside exhaust components and combustion chambers where the thermal radiation is of only minor importance. The ~150 µm thick nano grained 8YSZ TBC also was found to reduce the heat lost to the cooling water jacket by 5 to 10% which raised the thermal efficiency by 2 to 4%.

8.9.2: Performance of engine mounted with nano α-Al_2O_3 coated gudgeon pin

Figure 26 shows the Specific Fuel Consumption (SFC) of engine with nano α-Al_2O_3 coated gudgeon pin with 100 hours of engine run time. Performance curve of the baseline engine was used to compare the performance of the modified engine.

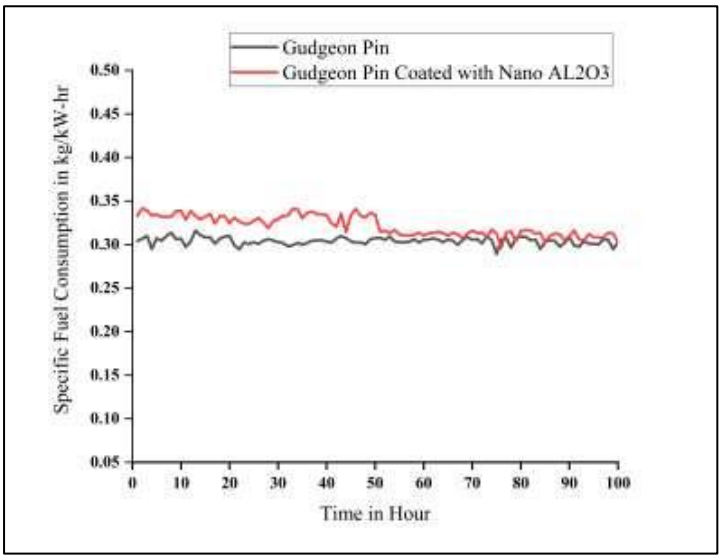


Figure 26 - Nano α-Al_2O_3 coated gudgeon pin in diesel engine –SFC vs. time graph

A spike in the SFC was observed during the first 20 hours of running the engine: it increased from the start till up to 20 hours of operation most likely due to the friction induced by the coated surface. Subsequently the SFC reduced and reached the values that matched with the SFC of the un-modified engine and remained unchanged for the next 80 hours of operation. The Brake power remained unchanged in both the cases (without and with coated component) and at the end of the test, the coated gudgeon pin was visually inspected and the coating was intact thereby establishing its good quality was established.

9. CONCLUSIONS

The following conclusions were drawn from this research work.

a. The challenges encountered in the development of Atmospheric Plasma Sprayed Coatings of 8% Yttria stabilized zirconia (8YSZ) and α-Alumina (α-Al_2O_3) nano coatings were successfully addressed and overcome. The specialty and novelty of the 150 thick developed coatings is that they possess nano grained microstructure, which do not show any signs of deterioration when subjected to thermal fatigue tests at 900°C (8YSZ on steel substrate) and ambient at room temperature and wear tests (α-Al_2O_3 on SS or Al-Si alloy substrates). The plasma spray powder and coatings development was followed by demonstration of their usefulness in a single cylinder diesel engine.
b. Starting from commercial nano powders, the two compositions were spray dried to obtain agglomerated powders that were free flowing and could be used as plasma sprayable powders (feed stock) with 45 to 50% deposition efficiency. Gaining an understanding and adoption of most effective spray drying parameters with usage of suitable binder comprised an important milestone in this research and developmental work facilitated by extensive literature study. An off shoot of the work was the synthesis of 8YSZ nano powders in the lab by sol-gel method which ensured there was no break in the supply of the raw material, especially the expensive 8YSZ composition. Starting from zirconium oxy-chloride, about 80 grams of nano 8YSZ (30 and 90 nm size) could be synthesized per batch in ~8 hours. The developed plasma sprayable powders exhibited adequate flowability (46 - 48 grams/minute) and deposition efficiency (~10 grams per pass) and the agglomerated individual powder particles were ~20 to 50 µm.
c. After detailed studies involving parameter modification where the initial process parameters were guided by literature and experimentation, the powders were plasma spray coated onto stainless steel and Aluminium -11 Silicon alloy substrates. The milestone that was successfully achieved was the development of a process methodology to plasma spray coat 120 to 150 µm 8YSZ coatings for thermal barrier coatings (TBC) applications and α-Al_2O_3 coating, suitable for wear resistance applications: the novelty in both the coatings being nano grained microstructure. In addition to structural phase and metallographic analysis (via polished metallographic cross section), the coatings successfully withstood the relevant (pertinent to the application) characterization tests. The tests were: Thermal fatigue resistance, micro hardness, wear tests, scratch indentation/friction resistance, structural phase and micro structure after thermal fatigue test (for 8YSZ) etc. Well

adherent, several tens of microns thick coatings with nano grained microstructure development in both the coats were the most important achievement. Process parameter optimization via judicially chosen experimentation enabled this development.

d. The plasma spray parameters used to fabricate the coatings on the substrates were used to deposit ~150 µm thick coatings on actual diesel engine components: piston head for 8YSZ TBC (Al-11 Si substrate) and gudgeon pin for α-Al_2O_3 (steel substrate) coatings deposition. This was followed by incorporating the components in the engine, and carrying out performance evaluation by running the engine for 100 hours at maximum load. The performance of the modified engine (with coated components) was compared with the Original Equipment Manufacturer (OEM) engine with as received components. A significant increase (~ 22%) in BSFC in the engine with 8YSZ coated piston was a major achievement. It may be worthwhile to highlight that diesel engine with conventional 8YSZ TBCS (micron grained microstructure) have been reported to exhibit performance enhancement (BSFC) of practically not more than 10%. All efforts were taken to ensure the experiments in this research work were error-free and were performed under the direct supervision of trained experts.

This research work resulted in 4 Indian patents (published), 3 journal papers (published in Scopus indexed) and 6 International conference presentations.

Scope for Future work

The nano coatings development in this research work has been achieved by a combination of extensive literature survey (limited resources were available) followed by narrowing down of spray drying and plasma spray coating process parameters to represent the most likely parameters' with potential to be developed into good quality coatings. Several iterations via experimentations had to be carried out to evolve a set of process parameters that generated superior quality coatings. Usage of analytical tools such as Taguchi and RSM (Response surface methodology) methods will be highly beneficial to arrive at optimized process parameters in a highly organized manner.

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PUBLICATIONS & PROCEEDINGS

I. Papers in Journals

1. **Gowtham Sanjai S**, Ratan Pinto, Parvati Ramaswamy "Plasma Sprayed Nano Refractory coatings". Institute of Physics (IOP) Conference series (Scopus indexed journals): 577(2019) 012100, Pp. 1-10. doi.10.1088/1757-899X/577/1/012100

2. **Gowtham Sanjai S**, Anantha Krishna B, Sreejai Srideep, M Sai Sumanth, Parvati Ramaswamy "Process Development to synthesize Plasma Sprayable Powders from Nano Alumina Ceramic Powders". Materials Today: Proceedings (Elsevier), 19 (2019) Pages708-714 doi. org/10.1016/j.matpr.2019.07.757

3. **Gowtham Sanjai S**, Sreejai Srideep, Anantha Krishna B, M Sai Sumanth and Parvati Ramaswamy: "Synthesis of Yttria-Stabilized Zirconia Nano Powders for Plasma Sprayed Nano Coatings", Materials Today: Proceedings (Elsevier), 22(2020) Pages 1253-1263 doi.org/10.1016/j.matpr.2020.01.418

II. Seminars / Conferences / Workshops Attended/Presented (Related To Research Work)

1. **Title:** "Plasma Sprayed Nano Refractory Coatings".

Authors: **Gowtham Sanjai S**, Ratan Pinto and Parvati Ramaswamy

Oral Presentation at International Conference on Advances in Materials and Manufacturing Applications (IConAMMA 2018) during August 16-18, 2018 organized by Amrita School of Engineering, Bangalore

2. **Title:** "Synthesis of Yttria-Stabilized Zirconia Nano Powders for Plasma Sprayed Nano Coatings".

Authors: **Gowtham Sanjai S**, Anantha Krishna B, Sreejai Srideep, M Sai Sumanth and Parvati Ramaswamy

Oral Presentation at the International Conference on Manufacturing, Modeling and Material Science–ICMMM 2019 during March 29-31, 2019 Organized by Vellore Institute of Technology, Vellore

3. **Title:** "Process Development to synthesize Plasma Sprayable Powders from nano Alumina Ceramic Powders".

Authors: Gowtham Sanjai S, Anantha Krishna B, Sreejai Srideep, M Sai Sumanth and Parvati Ramaswamy

Oral Presentation at 1st International Conference on Manufacturing, Material Science and Engineering –ICMMSE 2019 during August 16-17, 2019 Organized by CMR Institute of Technology, Hyderabad

4. **Title:** "Study on the Influence of pH concentration on the Yield and Particle Sizes of Yttria Stabilized Zirconia Nano Powders via Sol-Gel Synthesis".

Authors: Gowtham Sanjai S, Sreejai Srideep, Anantha Krishna B, M Sai Sumanth and Parvati Ramaswamy

Oral Presentation at International Conference on Advances in Materials and Manufacturing Applications (IConAMMA 2019) during August 29-31, 2019 organized by Amrita School of Engineering, Bangalore

5. **Title:** "Synthesis of Yttria -stabilized Zirconia Nanopowders and Plasma Sprayable Powders from Ceramic Nano Powders to serve as Thermal Barrier Coatings in Automobile Industry"

Authors: Gowtham Sanjai S, Sreejai Srideep, Anantha Krishna B and Moturu Sai Sumanth

Poster Presentation at International Symposium on Advanced Materials for Industrial and Societal applications NMD-ATM 2019 November 13 - 16, 2019 organized by IIM, Trivandrum Chapter, Thiruvananthapuram.

6. **Title:** "Study on the Sprayability of Nano Yttria Stabilized Zirconia Plasma Sprayable Powders for Thermal Barrier Coatings Applications".

Authors: Gowtham Sanjai S and Parvati Ramaswamy

Oral Presentation at 2nd International Conference on Nano Science and Nanotechnology (ICNAN 2019) November 29 - December 01, 2019 organized by VIT, Vellore.

III. PATENTS (PUBLISHED)

1. Nano α-Al_2O_3 particles agglomerated by spray drying to produce free flowing powders suitable for plasma spray coating, Application No. 202141035836 A, Published on 20 August 2021.

   Inventors: **Gowtham Sanjai S**, Dr Parvati Ramaswamy

2. A method to obtain up to 150µ thick nano-structured α- Al_2O_3 coatings by plasma spraying, Application No. 202241005098 A, Published on 18 February 2022.

   Inventors: **Gowtham Sanjai S**, Dr Parvati Ramaswamy

3. Synthesis of spray dried Nano 8YSZ Plasma sprayable powder and plasma sprayed thermal barrier coatings with nano grained microstructure, Application No. 202241011004, Published on 11 March 2022.

   Inventors: **Gowtham Sanjai S**, Dr Parvati Ramaswamy

4. Performance of diesel engine enhanced by employing 150µm to 170µm thick plasma sprayed 8YSZ nano grained coating on piston head, Application No. 202241033004, Published on 17 June 2022.

   Inventors: **Gowtham Sanjai S**, Kiran K, Dr Parvati Ramaswamy, Dr Gurumoorthy S Hebbar